

In presenting the dissertation as a partial fulfillment of the requirements for an advanced degree from the Georgia Institute of Technology, I agree that the Library of the Institute shall make it available for inspection and circulation in accordance with its regulations governing materials of this type. I agree that permission to copy from, or to publish from, this dissertation may be granted by the professor under whose direction it was written, or, in his absence, by the Dean of the Graduate Division when such copying or publication is solely for scholarly purposes and does not involve potential financial gain. It is understood that any copying from, or publication of, this dissertation which involves potential financial gain will not be allowed without written permission.

1000 ... 5000 ... 10000 ...
v ... 0 ... 0 ...

7/25/68

Original Page Numbering Retained.

THE PHOTOCHEMISTRY OF BENZOTRIAZINE DERIVATIVES

A THESIS

Presented to

The Faculty of the Division of Graduate
Studies and Research

by

Meng-sheng Ao

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
in the School of Chemistry

Georgia Institute of Technology

September, 1970

THE PHOTOCHEMISTRY OF BENZOTRIAZINE DERIVATIVES

PART I

PHOTOCHEMICAL SYNTHESIS OF
BENZOCYCLOPROPENONE

PART II

PHOTOCHEMICAL SYNTHESIS OF
SUBSTITUTED 2H-BENZOTHAZETE-1,1,-DIOXIDE

Approved:

C. R. M. D.
Chairman
A. D.

Date approved by Chairman: Sept. 24, 1970

ACKNOWLEDGMENTS

The author is most grateful to Dr. Edward M. Burgess for his invaluable guidance, counsel during the course of this study and in preparation of this dissertation, and provision of financial support through grants from the National Science Foundation.

The reading of this thesis by Drs. Drury S. Caine, III and Charles L. Liotta is greatly acknowledged. The author wishes to thank Dr. E. A. Taylor for his assistance with the experimental work in Part I, and reading the manuscript of this thesis. Special thanks are due to Mr. George S. Turner for his obtaining the mass spectral data.

Finally, the author is indebted to his wife for her encouragement during the entire period of study.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	11
LIST OF CHARTS	v
LIST OF TABLES	vi
LIST OF FIGURES	vi

PART I

Chapter

I. INTRODUCTION	1
II. EXPERIMENTAL	4
Apparatus and Techniques	
Preparation of 3- <u>p</u> -Tolylsulphonylamino-1,2,3-benzotriazin-4(3 <u>H</u>)-one (VIa)	
Preparation and Irradiation of Lithium 3- <u>p</u> -Tolylsulphonylamino-1,2,3-benzotriazin-4(3 <u>H</u>)-one (VIIa)	
Preparation of 6-Chloro-3- <u>p</u> -tolylsulphonylamino-1,2,3-benzotriazin-4(3 <u>H</u>)-one (VIb)	
Preparation and Irradiation of Lithium 6-Chloro-3- <u>p</u> -tolylsulphonylamino-1,2,3-benzotriazin-4(3 <u>H</u>)-one (VIIb) in Various Solvents	
III. DISCUSSION OF RESULTS	11
IV. CONCLUSIONS	16
LITERATURE CITED	18

PART II

Chapter

I. INTRODUCTION	19
II. EXPERIMENTAL	33
Apparatus and Techniques	
2-Phenyl-2 <u>H</u> -1,2,3,4-benzothiatiazine-1,1-dioxide (XXXa)	
Thermolysis of 2-Phenyl-benzothiazete-1,1-dioxide (XXXIa)	
Irradiation of Phenothiazin-5,5-dioxide (XXXVIa)	

TABLE OF CONTENTS (Continued)

Chapter	Page
2- <u>t</u> -Butyl-2 <u>H</u> -1,2,3,4-benzothiatriazine-1,1-dioxide (XXXb)	
2-(2,6-Dimethylphenyl)-2 <u>H</u> -1,2,3,4-benzothiatriazine-1,1-dioxide (XXXc)	
2-(2,6-Dimethylphenyl)-benzothiazete-1,1-dioxide (XXXIc)	
2-Benzhydrylideneamino-2 <u>H</u> -1,2,3,4-benzothiatriazine-1,1-dioxide (XXXd)	
3-Benzhydrylideneamino-3 <u>H</u> -2,1,3-benzoxathiazole (XLIId)	
III. DISCUSSION OF RESULTS.	45
IV. CONCLUSIONS.	63
LITERATURE CITED.	64
VITA.	67

LIST OF CHARTS

PART I

Chart	Page
1. Synthetic Route to Compounds VIa and VIb	11
2. Irradiation Products of Compound VIIa and VIIb	12
3. Mechanism Suggested for Photolysis of III and XI	14

PART II

Chart	Page
1. Synthetic Route to Compound XXXa, XXXb, XXXc and XXXd. . . .	46
2. Photochemical or Thermal Decomposition of the Triazine XXXa. . .	48
3. Mechanism of Formation of Carbazole (XXXV)	49
4. Mechanism of Phenothiazine Dioxide (XXXVIa) Formation. . . .	50
5. Photochemical or Thermal Decomposition of the Triazine XXXb. . .	52
6. Photochemical or Thermal Decomposition of the Triazine XXXc. . .	54
7. Photochemical or Thermal Decomposition of the Triazine XXXd. . .	58
8. Mechanism of Photochemical Formation of XLIIId.	60
9. Mechanism of Thermal Formation of XLII and XLIII	61

LIST OF TABLES

PART I

Table	Page
1. Delocalization Energy (DE) of Cyclopropenones As Calculated from Huckel Theory, and the Increase (ΔDE) on Phenyl Substitution	2

PART II

Table	Page
1. The Total Energy (E_T) of Some Heterocycles IIa As Function of the $\sigma(E_\sigma)$ and $\pi(E_\pi)$ -electron Structure.	31

LIST OF FIGURES

PART I

Figure	Page
1. Photolysis Apparatus (I)	5
2. Photolysis Apparatus (II).	6

PART I

CHAPTER I

INTRODUCTION

Interest in the chemistry of nonbenzoid unsaturated cyclic compounds has steadily increased since Hückel's rule concerning aromaticity was introduced into the literature three decades ago. According to this rule, any planar cyclic conjugated π -electron system which contains $(4n+2)$ ($n = 0, 1, 2, \dots$) π -electrons possesses unusual electronic stability or aromaticity. The cyclopropenium cation, cyclopentadienide anion, the cycloheptatrienium cation, [14]annulene and [18]annulene, for example, should be aromatic; but cyclobutadiene, cyclooctatetraene, and [12]annulene should be non-aromatic even if they are planar.

The simplest member ($n = 0$) in the series of $(4n+2)$ π -systems is the cyclopropenium cation, which has a large calculated delocalization energy of 28. Cyclopropenone and its derivatives can have a cyclopropenium ion (Eq. 1) resonance contribution to the electronic ground state which results in some π -electron delocalization energy (Table 1).

Eq. 1

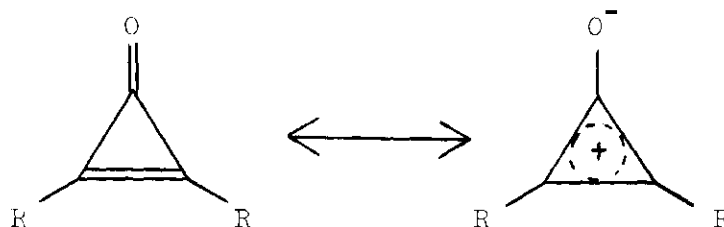
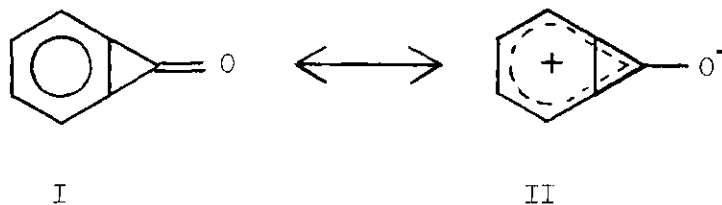


Table 1 (1). Delocalization Energy (DE) of Cyclopropenones As Calculated from Huckel Theory, and the Increase (Δ DE) on Phenyl Substitution.

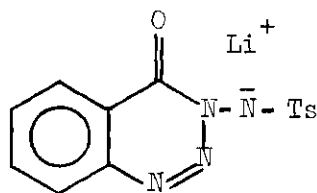
	DE (β)	Δ DE (β)
Cyclopropenone	1.35	
Phenylcyclopropenone	3.75	0.39
Diphenylcyclopropenone	6.15	0.79

However, it should be noted that the calculated delocalization energies take into account only this contribution of π -electrons towards the stability of the molecules. The calculations are unable to predict to what extent the ring strain energy would counterbalance the delocalization energy. Consequently, it was impossible to predict whether a large delocalization energy will make a cyclopropenone system sufficiently stable to permit its isolation. However, since diphenylcyclopropenone was made and found to be remarkably stable (1,2) in spite of its strained nature, interest has been growing in the synthesis of other cyclopropenone derivatives.



Benzocyclopropenone (I) which represents the fusion of a cyclopropenone and a benzene ring, should be more strained but electronically more stable due to the potentially homoaromatic resonance contributor (II) than benzocyclopropenes which has been isolated and found to be fairly stable. The former has been suggested as an intermediate ion in the thermal and mass spectral fragmentation of phthalic anhydride and indanetrione (3,4).

It was the purpose of this research to generate, trap or isolate, if possible, the reactive benzocyclopropenone from the photochemical decomposition of lithium 3-p-tolylsulphonylamino-1,2,3,-benzotriazin-4(3H)-one (VIIa).



VIIa

It had been shown in this laboratory that the thermolysis of VIIa at 220° in triglyme containing anthracene gives a 30% yield of benzyne-anthracene adduct, triptycene. A possibility exists that benzyne may result from the decarbonylation of an intermediate benzocyclopropenone after two moles of nitrogen and lithium p-toluenesulfinate have been lost from VIIa at high temperature. Hence, exploration of the photolytic decomposition instead of a high temperature thermolysis of VIIa seemed to provide a promising route to benzocyclopropenone.

CHAPTER II

EXPERIMENTAL

Apparatus and Techniques

Mass spectra were obtained using a Varian Associates Model M-66 medium resolution mass spectrometer. All exact mass determinations reported agree to within 0.005 of the calculated value. Nuclear magnetic resonance spectra were acquired using Varian A-60 spectrometer unless otherwise specified, deuteriochloroform containing one percent of tetramethylsilane (TMS) as an internal standard was used as solvent. Chemical shifts are reported in units of τ ($\tau = 10 - \sigma$). The abbreviations s, d, t, q and m refer respectively to singlet, doublet, triplet, quartet and multiplet nmr signals. Infrared spectra were obtained on a Perkin-Elmer Model 457 spectrophotometer using 0.2 mm sodium chloride cells with chloroform as the solvent. Only the infrared absorptions which are germane to structure conclusions are listed. Ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer using one centimeter balanced cells with 95% ethanol as the solvent. Gas chromatographic analyses were performed on a Hewlett-Packard Model 402 flame ionization gas chromatograph using a 4 ft. x 3 mm. glass column packed with Ucon polar coated firebrick. Thiophene free benzene was used. Prior to use all hydrocarbon solvents were distilled and the first portions of the distillate were discarded and tetrahydrofuran was distilled from lithium aluminum hydride. Methanol was distilled from magnesium methoxide before

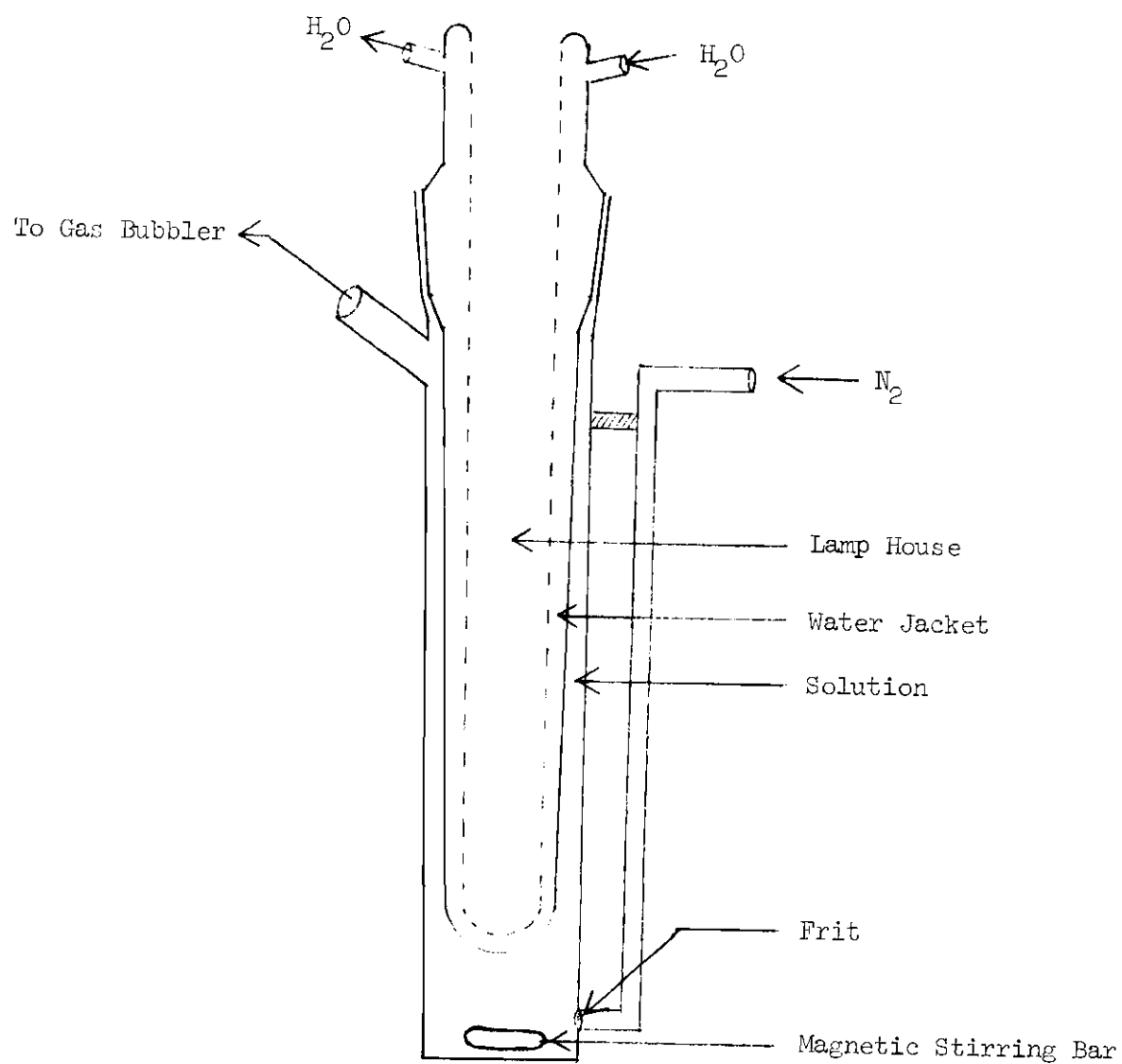


Figure 1. Photolysis Apparatus (I)

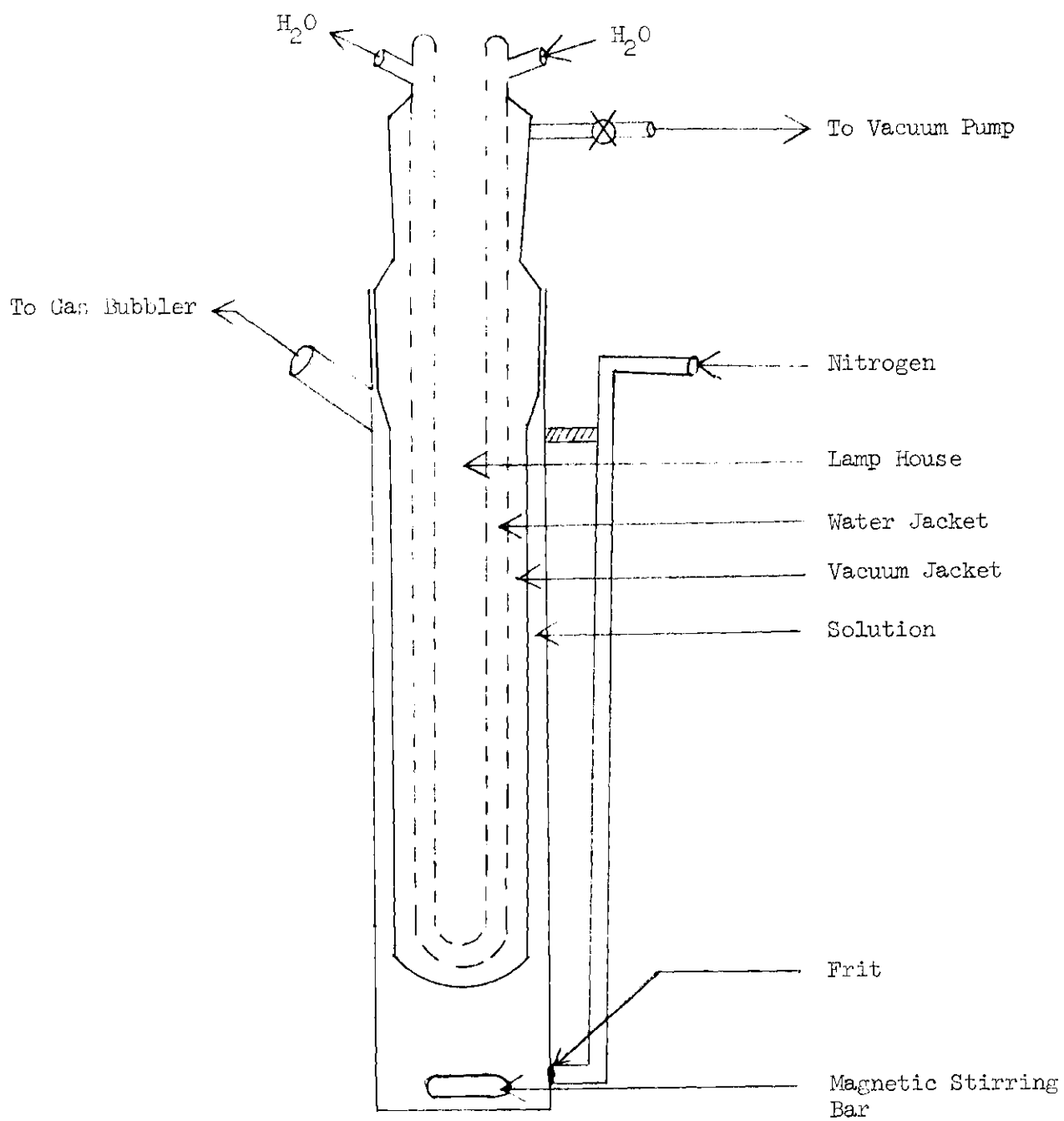


Figure 2. Photolysis Apparatus (II)

use. Melting points were determined on Thomas Hoover capillary melting point apparatus and are uncorrected. Solvent evaporation under reduced pressure was accomplished with a Büchi Rotavapor. A Hanovia 550 watt or 450 watt high pressure mercury vapor lamp was used for irradiations. The lamp was placed in Vycor water jacket, which was, in turn, fitted inside a Pyrex reaction vessel (Fig. 1). The resulting annular space had a capacity of about 250 ml and was filled to the neck with the solution to be photolyzed. Cold water was circulated through the water jacket during the photolysis at a rate to maintain the magnetically stirred solution at a temperature of 30°.

A stream of dry nitrogen was admitted through the frit into reaction mixtures before irradiation. The irradiation at -78° was carried out in an apparatus similar to the one described previously except having an evacuated space between the water jacket and the reaction vessel (Fig. 2). The reaction mixture was cooled in a dry ice-acetone bath. Thin-layer chromatography was carried out using microscopic slides coated with silica gel G and iodine vapor was used to develop the components and in each case reported the liquid phase is indicated.

Experimental

Preparation of *p*-Toluenesulphonhydrazide of Anthranilic Acid (Va)

Compound Va was prepared according to the method of Barlin (5). The colorless crystalline material had a mp 196-7° [lit.(5)mp 197.5-198.5°].

Preparation of 3-P-Tolylsulphonylamino-1,2,3-benzotriazin-4(3H)-one (VIa)

A solution of Va (10 g, 0.033 mole), 200 ml of water and 15 ml of concentrated hydrochloric acid was cooled with stirring in an ice bath. Sodium nitrite (4.5 g, 0.066 mole) in 10 ml of water was added at once to this solution. After stirring at 0° for 15 minutes the precipitate of VIa was collected by filtration, then washed with cold water and dried. Pure sample of VIa was obtained by crystallization from benzene to give 9.4 g (90%) of colorless needles: mp 204-6° (dec); nmr (DMSO-d₆) τ 7.57 (s, 3H), τ 1.60-2.72 (m, 9H). The mass spectrum showed a weak molecular ion at m/e 316.

Preparation and Irradiation of Lithium 3-P-Tolylsulphonylamino-1,2,3-benzotriazin-4(3H)-one (VIIa)

To a suspension of 2 g (0.0064 mole) of VIa in 250 ml of dry methanol under a nitrogen atmosphere was added with stirring one equivalent of lithium hydride. After the hydrogen evolution ceased the resulting solution of VIIa was irradiated with a 550 watt Hanovia lamp using a Pyrex filter. Nitrogen was rapidly evolved from the reaction mixture during one hour. The solvent was then evaporated under reduced pressure and the residue was shown to consist of three products as determined by tlc (10% ethanol in benzene) with R_F value of 0.00, 0.26, 0.55. By triturating the residue with benzene, the product with the smallest R_F value separated, and was collected by filtration, the filtrate was further treated with hexane until no more precipitate formed. Collection of the total precipitate yielded 0.86 g (92%) of lithium p-toluene-sulphinate (VIII).

The product with R_F 0.26 crystallized from the above concentrated filtrate at 0° and was collected to afford 0.17 g (8%) of o-methoxybenzoic

acid p-toluene sulphonhydrazide (IXa): mp 179-180° (dec), ir (CHCl₃) 3318 (NH), 1692 (C=O), 1260, 1080 (C-O-C), 1338 and 1160 (SO₂) cm⁻¹; nmr (CDCl₃) τ 7.58 (s, 3H), τ 6.17 (s, 3H) τ 1.92-2.86 (m, 8H), τ 3.00-3.88 (broad, 2H); exact mass determination gave 320.088 (for C₁₅H₁₆N₂O₄S: 320.083 calculated). The third product (R_f 0.55) was identified as methyl benzoate (Xa) by gas chromatographic comparison with an authentic sample (52% yield).

Preparation of 5-Chloro-p-toluenesulphonhydrazide of Anthranilic Acid (Vb)

Compound Vb was prepared in a similar manner to that of Va. The colorless crystalline compound had mp 236-8° (dec).

Preparation of 6-Chloro-3-p-tolylsulphonylamino-1,2,3-benzotriazin-4(3H)-one (VIb)

A solution of Vb (11.2 g, 0.033 mole), 100 ml of water, 100 ml of acetic acid and 20 ml of concentrated hydrochloric acid was cooled in an ice bath with stirring. To this solution 4.5 g (0.066 mole) of sodium nitrite in 10 ml of water was added. After the mixture had been stirred at 0° for 20 minutes, 100 ml of cold water was added. The precipitate of VIb which resulted was collected, washed with cold water and dried. Pure VIb was obtained by crystallization from ethanol to give 10.9 g (95%) of colorless needles: mp 170-2° (dec); nmr (DMSO-d₆) τ 7.53 (s, 3H), τ 6.61 (broad, 1H), τ 1.61-2.81 (m, 7H); the mass spectrum showed a weak molecular ion at m/e 351.

Preparation and Irradiation of Lithium 6-Chloro-3-p-tolylsulphonylamino-1,2,3-benzotriazin-4(3H)-one (VIIb) in Various Solvents

To a suspension of 2 g (0.0057 mole) of VIb in 250 ml of dry methanol under nitrogen was added, with stirring, one equivalent of lithium hydride. The methanolic solution of VIIb was irradiated with

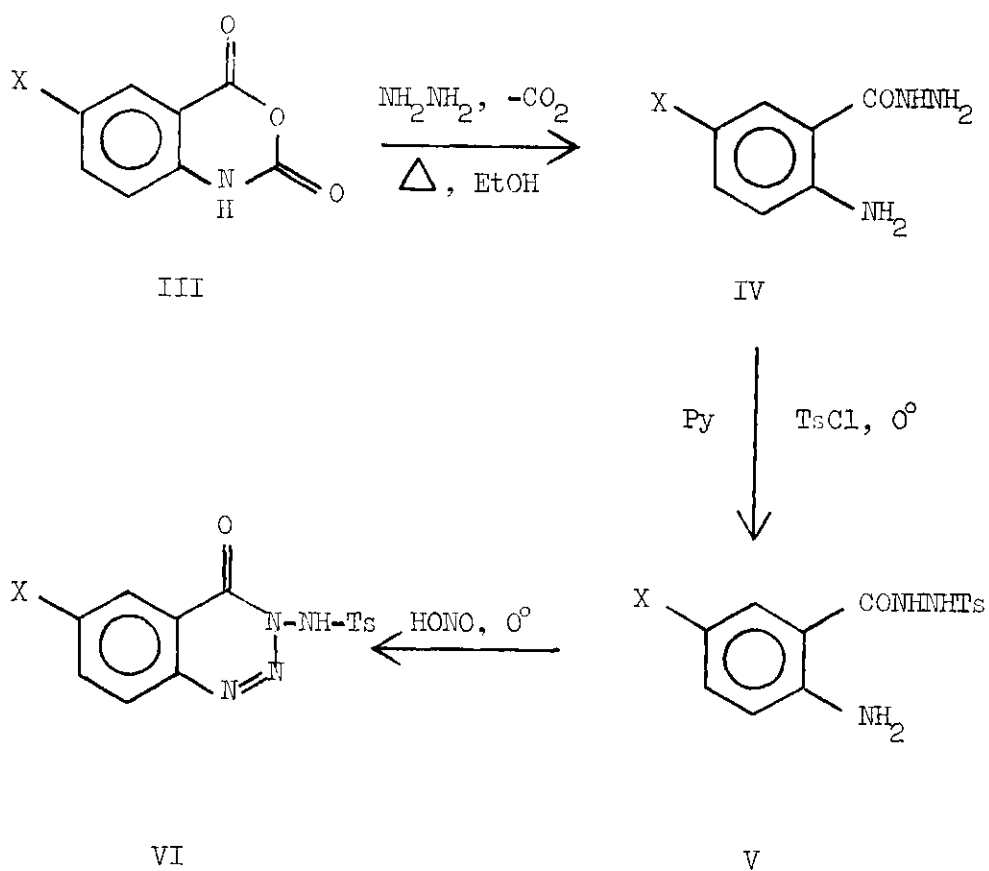
a 550 watt Hanovia lamp using a Pyrex filter. Nitrogen was evolved from the reaction mixture during 2 hours. Tlc (10% ethanol in benzene) indicated the formation of three compounds which were isolated by the procedure described for the irradiation of VIIa and identified as VIII (0.73 g, 90%), 5-chloro-2-methoxybenzoic acid p-toluenesulphonhydrazide (0.12 g, 6%) (IXb): mp 154-5° (dec); ir (CHCl₃) 3319 (NH), 1696 (C=O), 1246, 1082 (C-O-C), 1335, 1168 (SO₂) cm⁻¹, and methyl-p-chlorobenzoate (Xb) (42%) by gas chromatographic comparison with an authentic sample.

In another experiment, to a solution of 1 g (0.0029 mole) of VIb in 250 ml of dry benzene under nitrogen was added, with stirring, one equivalent of lithium hydride to give a benzene solution of VIIb. This solution was irradiated for 2 hours in the same manner as described previously. Nitrogen was slowly evolved from the reaction mixture. After removal of the precipitate of lithium p-toluenesulphinate and the solvent, the crude product (5%) by both gas chromatography and tlc (10% ethanol in benzene) was shown to be 4-chlorobenzophenone by comparison with an authentic sample.

CHAPTER III

DISCUSSION OF RESULTS

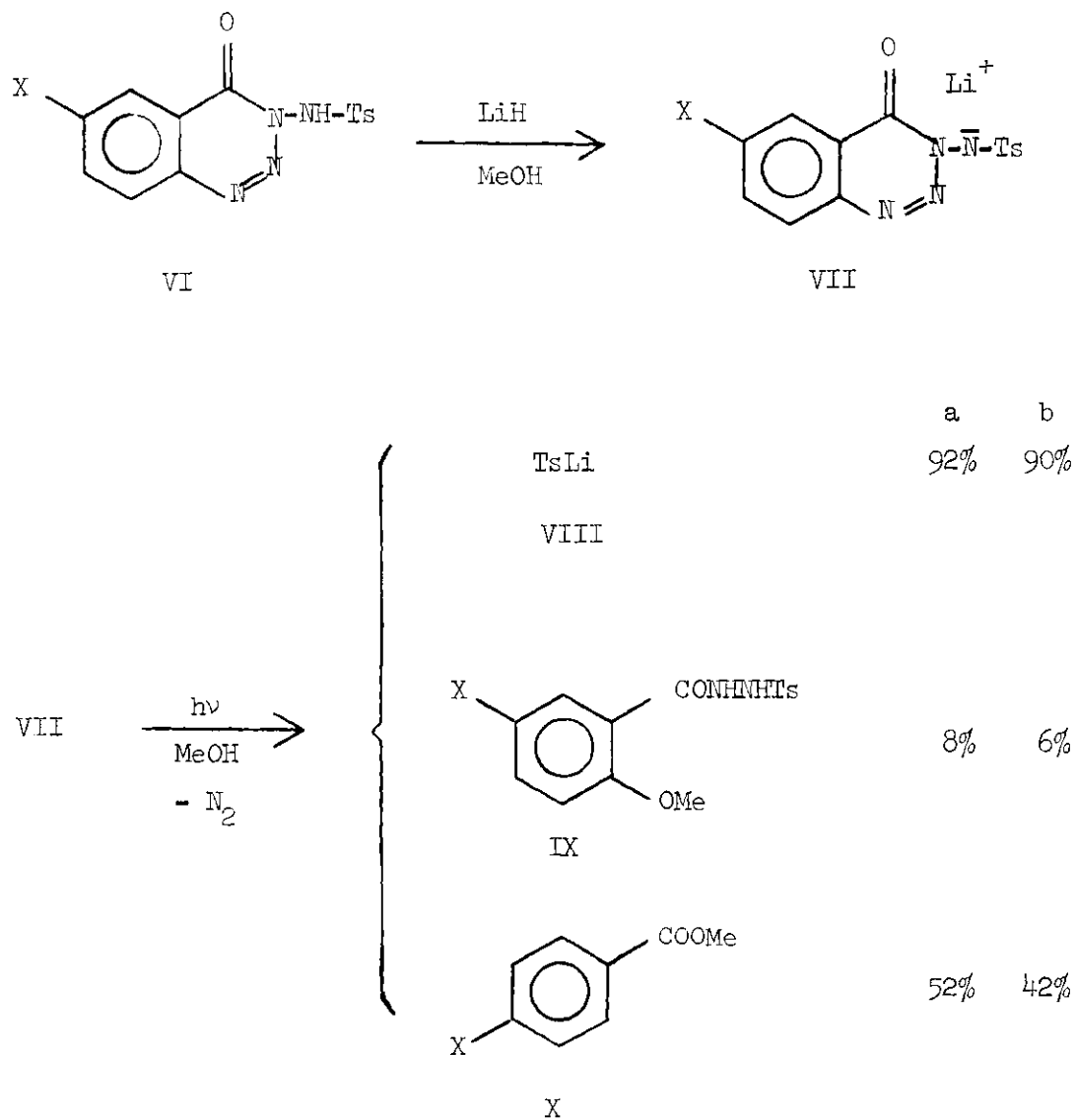
Chart I shows the synthetic routes to the starting materials and Chart II shows the resulting irradiation products and their percent yields.



a, X = H

b, X = Cl

Chart I. Synthetic Route to Compounds
VIa and VIb



a, X = H

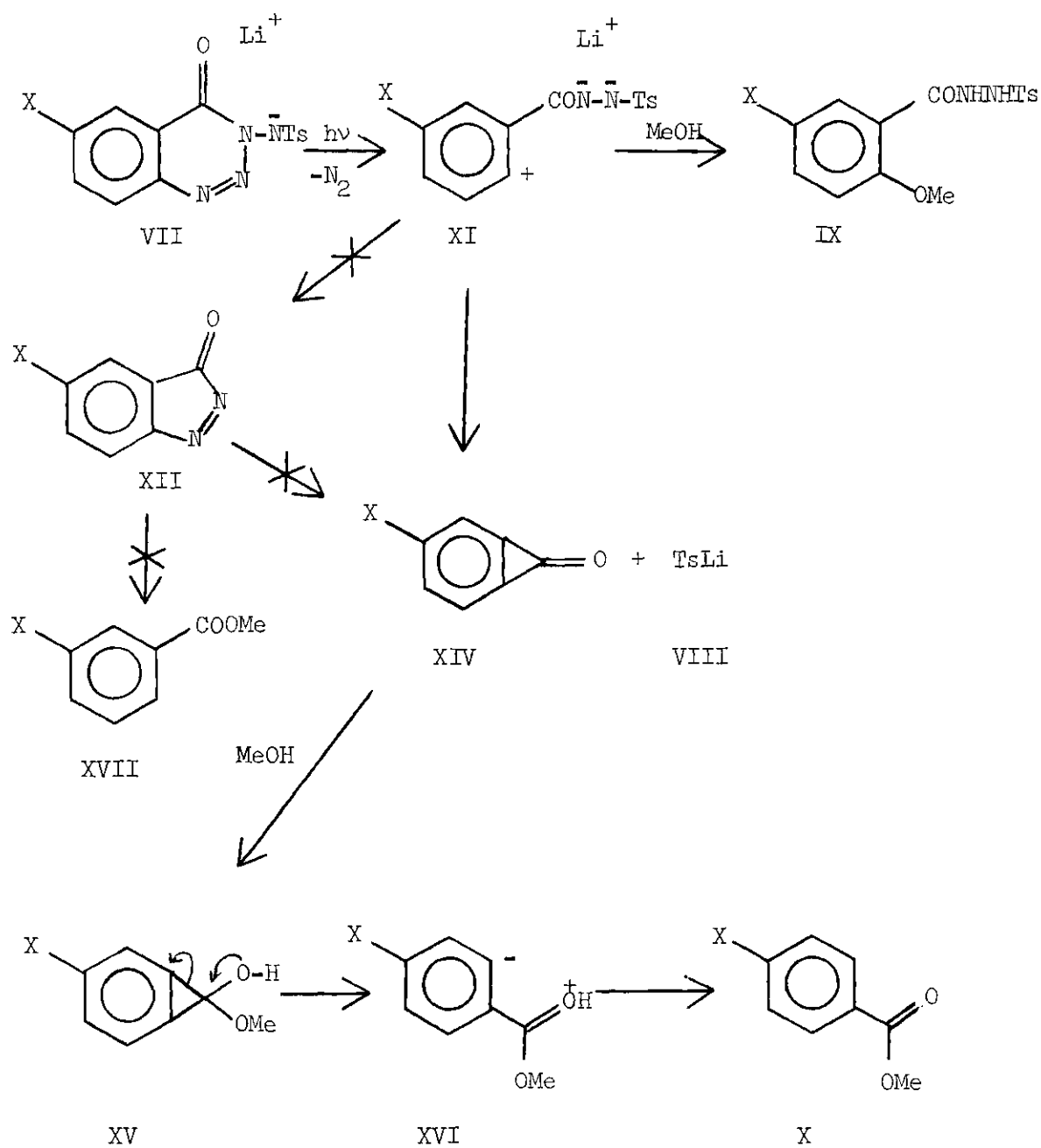
b, X = Cl

Chart II. Irradiation Products of Compound VIIa and VIIb

As indicated in Chapter I, the object of this research was to generate benzocyclopropenone. Clear mechanistic evidence for the intermediacy of benzocyclopropenone in the photolysis of both compound VIIa, VIIb was obtained.

Under ultraviolet excitation VII (λ_{max} 320 nm) loses one mole of nitrogen to form a dipolar intermediate XI, which may account for the formation of IX in the presence of methanol. The dipolar intermediate XI then collapses to 4-chlorobenzocyclopropenone (XIV) with formation of VIII. However, the possible intermediacy of XII, can be excluded from further considerations, since the known methanolysis product, methyl-m-chlorobenzoate (XVII), was not obtained (6). Compound XII is, therefore, not the precursor of methyl-p-chlorobenzoate (X), hence, an intermediate with the symmetry of XIV is responsible for occurrence of the rearranged product X. The nucleophilic addition of methanol to XIV leads to a hemiacetal XV which undergoes Favorskii ring-opening through a possible intermediate XVI to yield the product X. From strain relief considerations, the uncatalysed acetalization of benzocyclopropenone should be more exothermic than that of diphenylcyclopropenone (1,2). This rearrangement requires a intermediate resembling XVI where the inductive stabilization of the developing carbanionic center by the chloro-substituent is greatest.

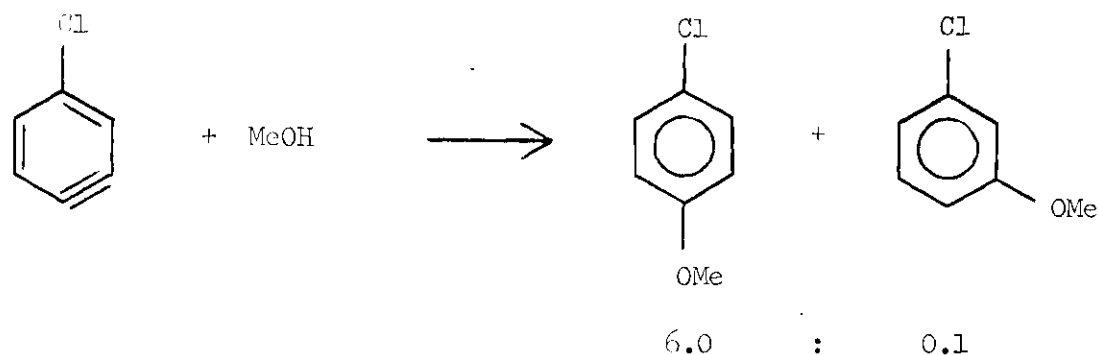
The arguments for the inductive stabilization by substituents have been previously invoked to explain isomer ratios in the addition of nucleophiles to unsymmetrically substituted dehydrobenzenes (Eq. 2) (7).



X = H or Cl

Chart III. Mechanism Suggested for Photolysis of VIIa and VIIb

Eq. 2



Such thermodynamic control provides for the predominant formation of the observed methyl-p-chlorobenzoate (X) (no meta isomer was detected by ir analysis).

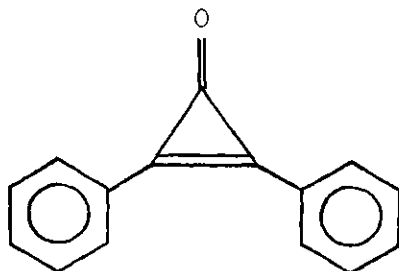
Further evidence in support the formation of benzocyclopropenone in such photodecompositions was observed in the photolysis of VIIb in dry benzene. A small amount of the rearranged product, 4-chlorobenzophenone (XVIII) was detected. The appearance of XVIII demands the addition of benzene to β -chlorobenzocyclopropenone.

Attempts to isolate benzocyclopropenone from the very complicated reaction mixture obtained from the irradiation of VIIa in dry tetrahydrofuran solution failed.

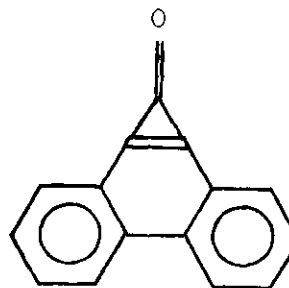
CHAPTER IV

CONCLUSIONS

The chloro-substituted and unsubstituted benzocyclopropenones were successfully generated in solution by the photochemical decomposition of VIIa and VIIb. They are a new class of reactive intermediates in chemical transformations, and were only detected by reaction with nucleophilic trapping agents. The strain ring energy may be a most crucial factor in determining the reactivity of various cyclopropenones. This can be seen as one compares the stability of diphenylcyclopropenone (XIX) and phenanthrocyclopropenone (XX).



XIX



XX

Diphenylcyclopropenone is a well known stable compound (1), whereas phenanthrocyclopropenone, which has a similar structure, is too reactive to be isolated (8). Surprisingly benzocyclopropenones do not thermally

expel carbon monoxide to form benzyne under our reaction conditions.* Whereas in the thermolysis of benzocyclopropenone at 220° carbon monoxide is, in a manner similar to diphenylcyclopropenone (1), eliminated in a nonconcerted fashion** (1,9) to form benzyne trapped as the anthracene adduct, triptycene.

A portion of this research has been reported previously (10).

* When VIIa was irradiated in anhydrous furan, a complicated mixture of products resulted which contained no detectable amount of a benzyne adduct.

** Cyclopropenone is a $4n$ π -electron system. According to the Woodward-Hoffmann rules, a $4n$ system is not allowed to undergo a thermally concerted fragmentation (9).

LITERATURE CITED*

1. A. W. Krebs, Angew. Chem. Internat. Ed., 4, 10 (1965).
2. R. Breslow, R. Haynie and J. Mirra, J. Amer. Chem. Soc., 81, 247 (1959).
3. R. F. C. Brown and R. K. Solly, Austral. J. Chem., 19, 1045 (1966).
4. E. K. Fields and S. Meyerson, Chem. Comm., 475 (1965).
5. G. B. Barlin, J. Appl. Chem., 12, 148 (1962).
6. E. F. Ullman and E. A. Bartkus, Chem. and Ind., 93 (1963).
7. R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, 1967, pp. 134-150.
8. T. L. Gilchrist and C. W. Rees, J. Chem. Soc., (C) 1763 (1969).
9. R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, 1970.
10. M. S. Ao, E. M. Burgess, A. Schauer and E. A. Taylor, Chem. Comm., 220 (1969).

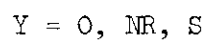
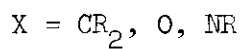
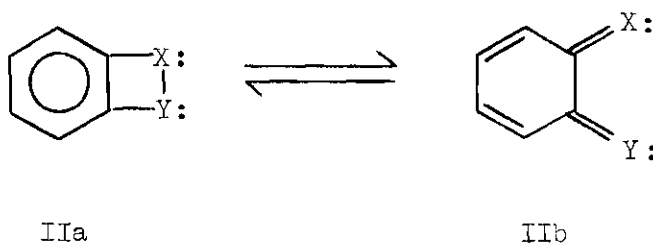
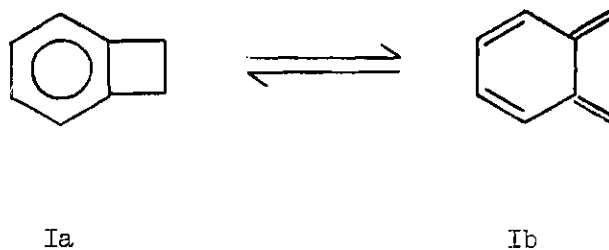
* For the complete title of all journals referred to, see Chemical Abstracts, 55, IJ (1961).

PART II

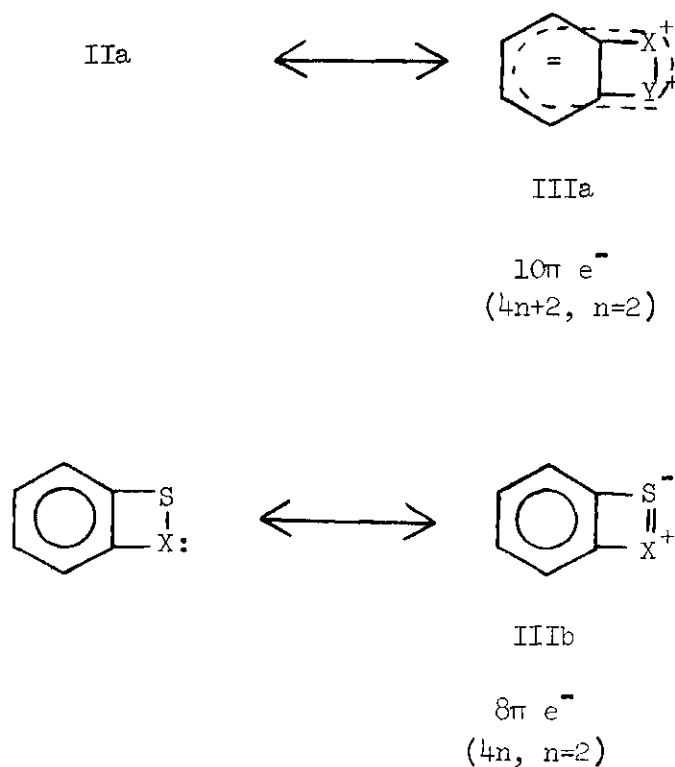
CHAPTER I

INTRODUCTION

Since the chemistry of benzocyclobutene (Ia) and its valence isomer, o-xylylene (Ib), has been disclosed (1), considerable speculative attention has been focused recently on the benzo-fused four-membered heterocyclic systems IIa, the hetero-analogs of Ia.

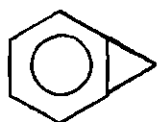


Compounds having the structure IIa are of theoretical significance because of the possibility of having either (a) a potential aromatic property (isoelectronic with naphthalene) represented by the resonance contributor IIIa or (b) a potential antiaromatic property (isoelectronic with cyclooctatetraene) represented by the resonance structure IIIb.

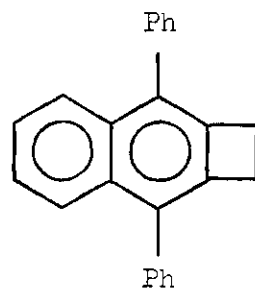


The possibility of reduction of aromatic properties (ring current) by fusion of small rings to benzenoid system is also of interest. This effect may arise from (a) rehybridization of the angular carbon atoms to accommodate the strain resulting from the imposed geometry and (b)

a decrease in the bond order of the [a] face carbon-carbon bond resulting from the symmetries of the filled molecular orbitals. Effect (a) does not appear to prohibit synthesis as evidenced by the recent isolation and reported properties of the ultimate in strained systems of this type, the benzocyclopropene (IIIc) (2). Effect (b) is important as judged from the reported properties of the isolable [b]naphthocyclobutadiene (IIIId) (3).

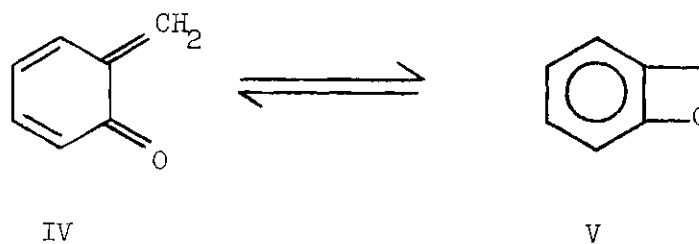


IIIc

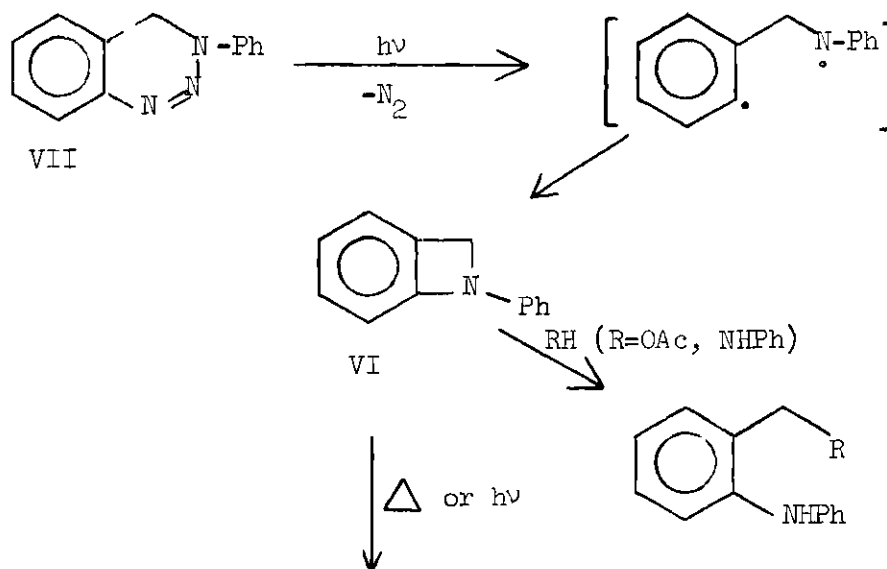


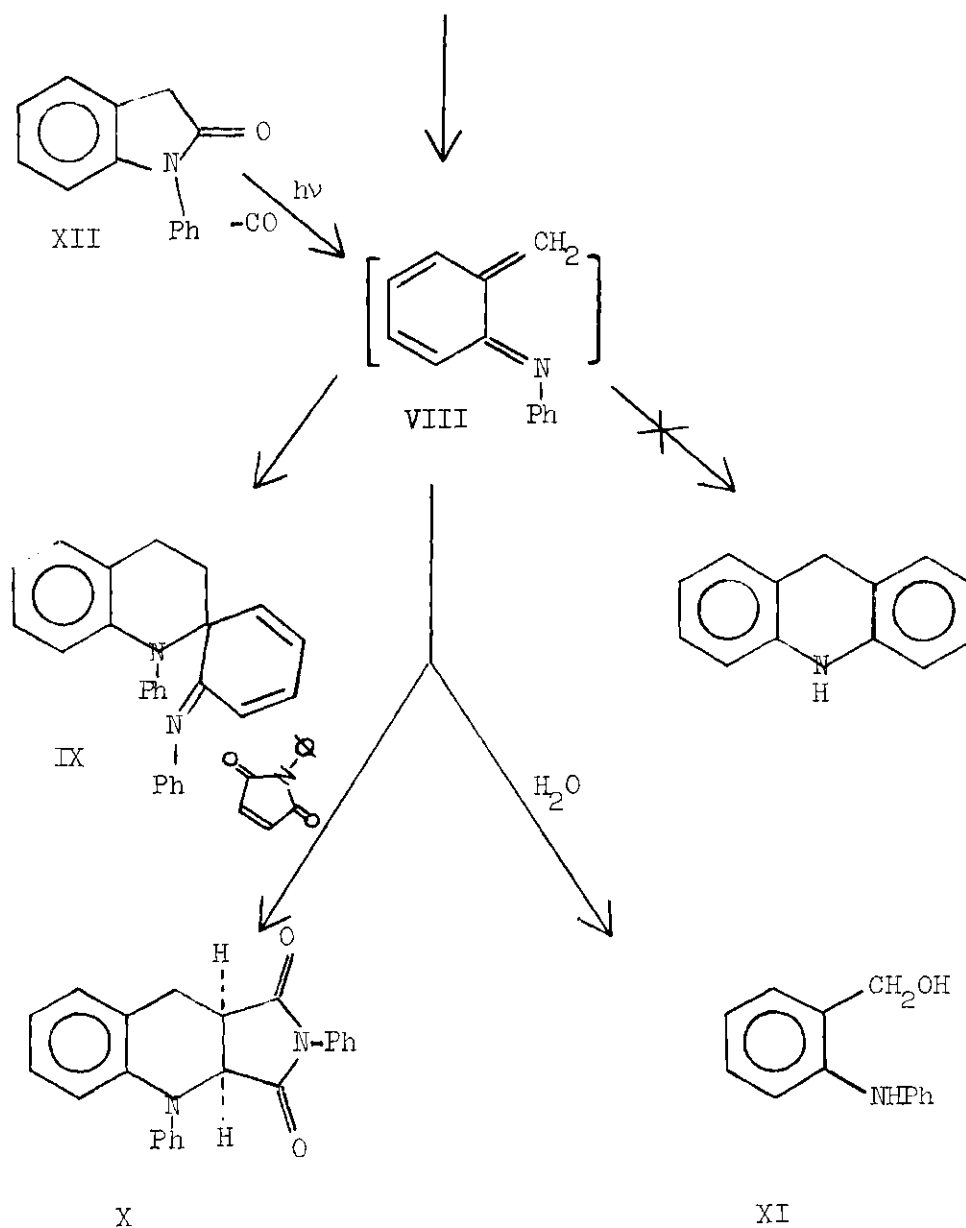
IIIId

The o-quinone methide (IV) has been reported (4) to have been prepared at low temperatures but no definitive chemical or physical information on the possibility that it may indeed be the 2H-benzoxete (V) has been presented. When IV (or V) is heated, a trimer of established constitution, results (5). The assigned structure for IV has received support from its observed conjugated addition of nucleophiles and cycloaddition to olefins. The role of variants of IV in biochemical processes has been reviewed and their intermediacy in the photoenolization of certain aromatic ketones reported (6).

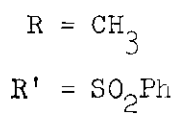
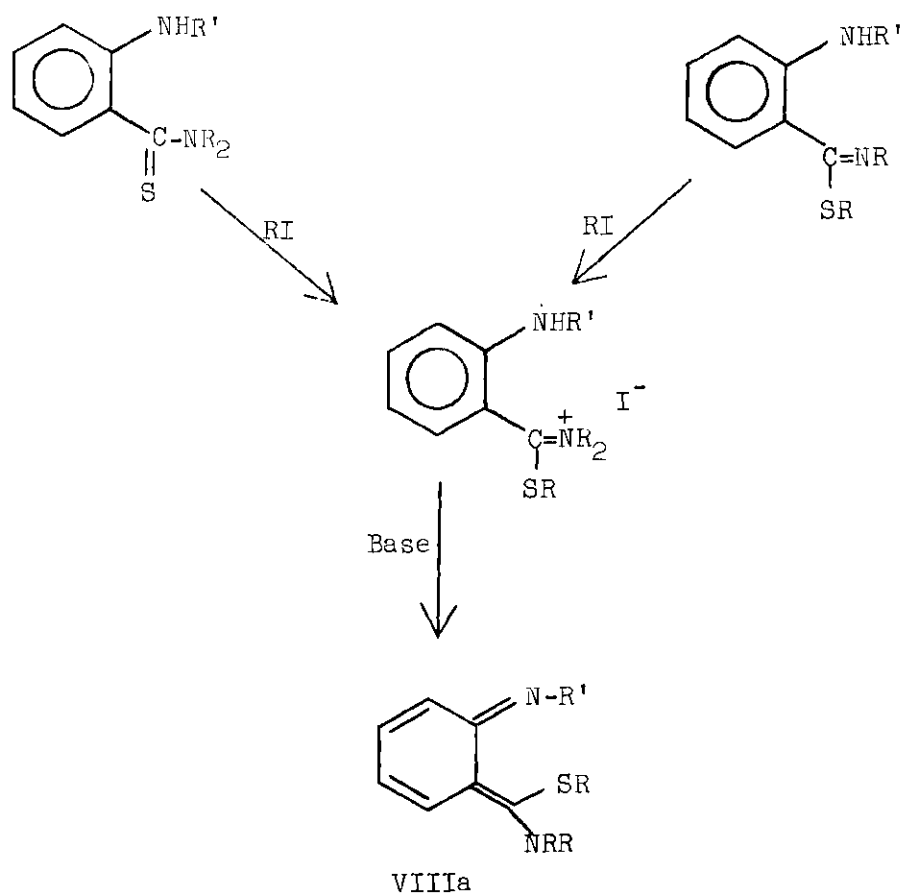


A novel synthesis of the first stable N-phenylbenzoazetine (VI) has been achieved through the photochemical decomposition of the 4H-benzotriazine VII to give a good yield of VI (7). The thermally or photochemically derived valence isomer of VI, o-quinone methide imine (VIII), was an intermediate in the formation of Diels-Alder adduct X, dimer IX, and nucleophilic addition product XI (7). The existence of this intermediate has received support from studies of the photo-decarbonylation of N-phenyloxindol (XII) (8,9).

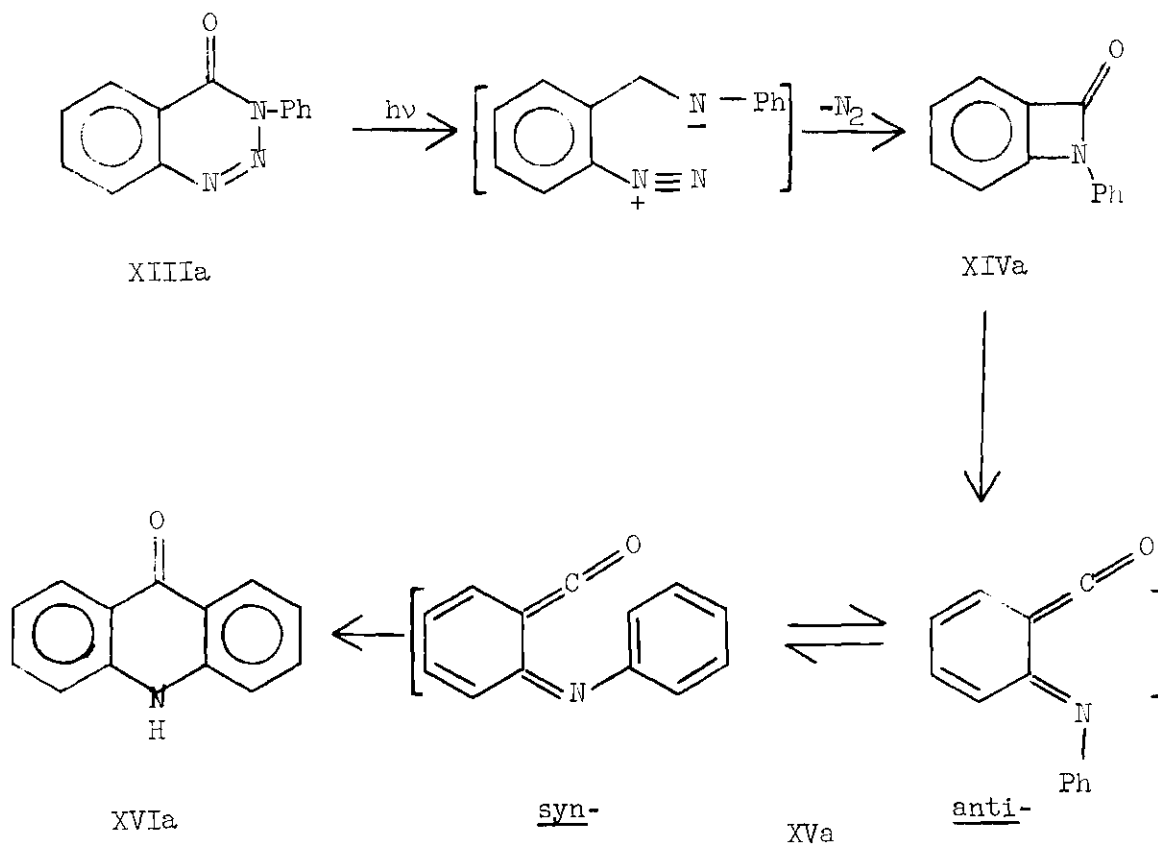




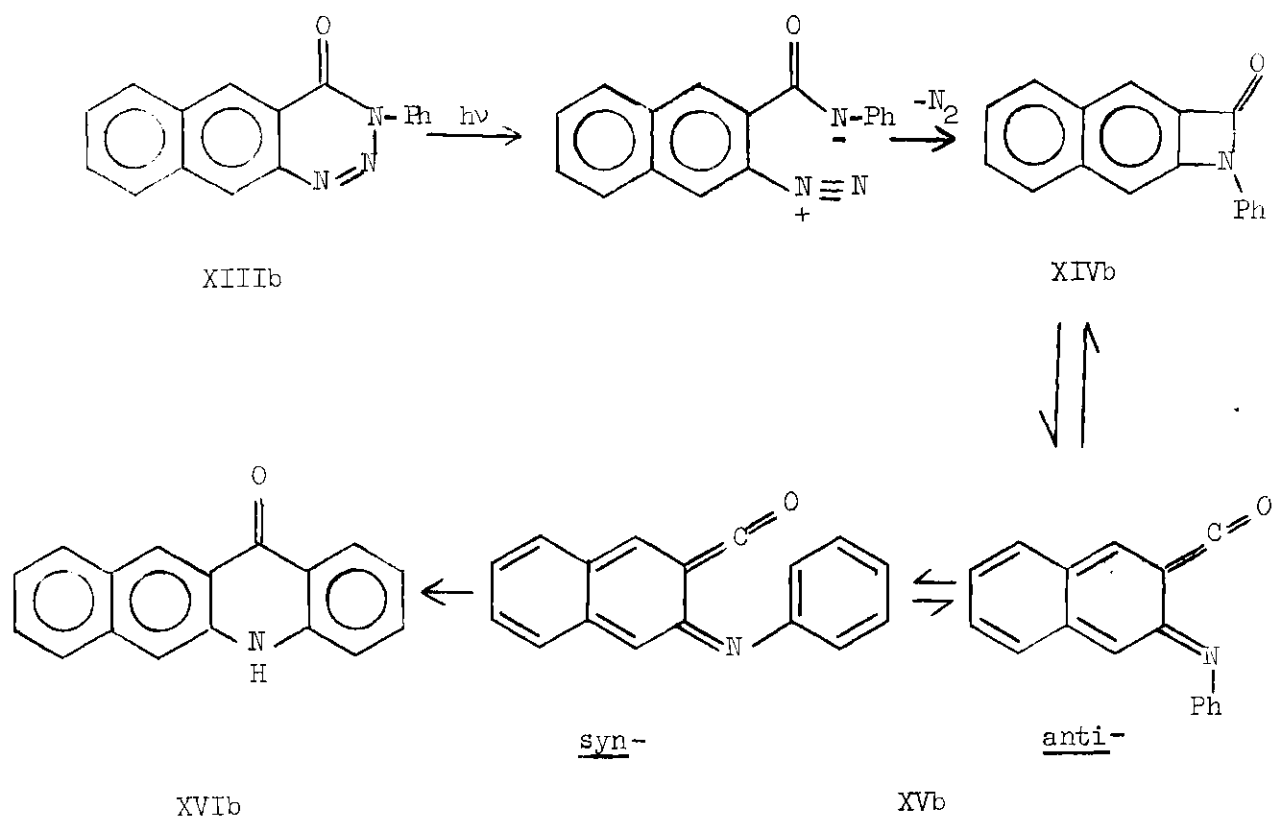
Derivatives of the valence isomer VIII, such as VIIIIa have also been isolated from non-photochemical reactions and found to be remarkably stable (10).



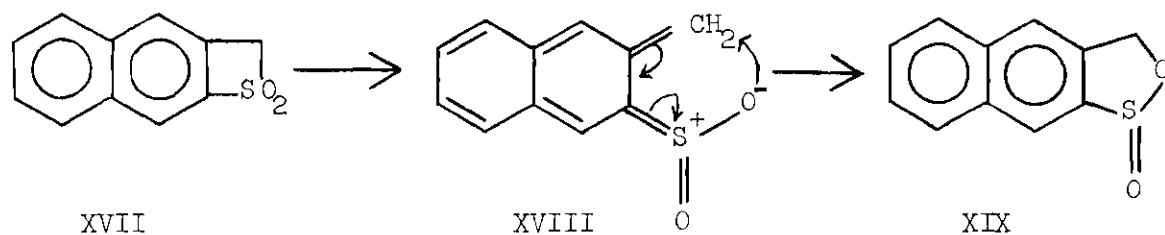
Studies of the benzo-fused azetinone system generated by the photolysis of benzotriazenone XIIIa and naphthotriazenone XIIIb have been carried out in aprotic solvents. Irradiation of XIIIa yielded acridone (XVIa) and no N-phenylbenzoazetinone (XIVa) could be isolated (11). However, the existence of XIVa in solution was proved by its reactions with nucleophiles and observation by ir spectroscopy (11).



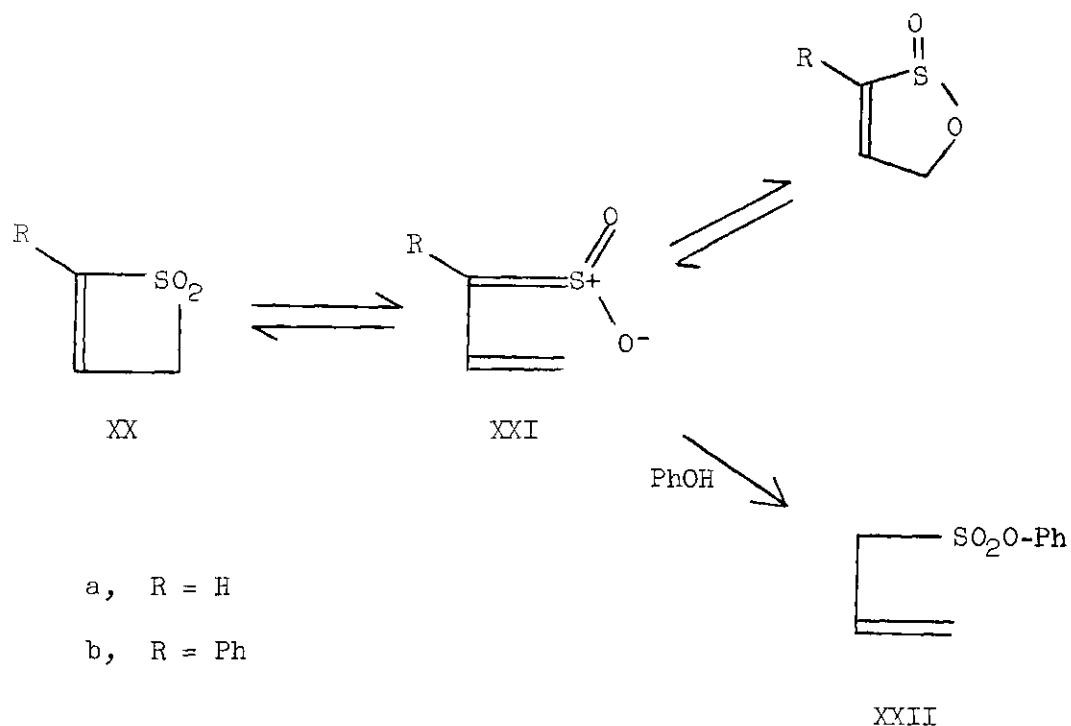
In the case of XIIIb, a stable crystalline N-phenylnaphtho[2,3-b]-azetinone (XIVb) was isolated in high yield (12). Benzo[d]acridone (XVIb) which was also a minor product in the initial photolysis of XIIIb, was the exclusive product when compound XIVb was further irradiated. To account for this transformation, the valence isomerization of XIVb to the intermediate ketene XVb, followed by cyclization of syn-XVb to XVIb is conceivable.



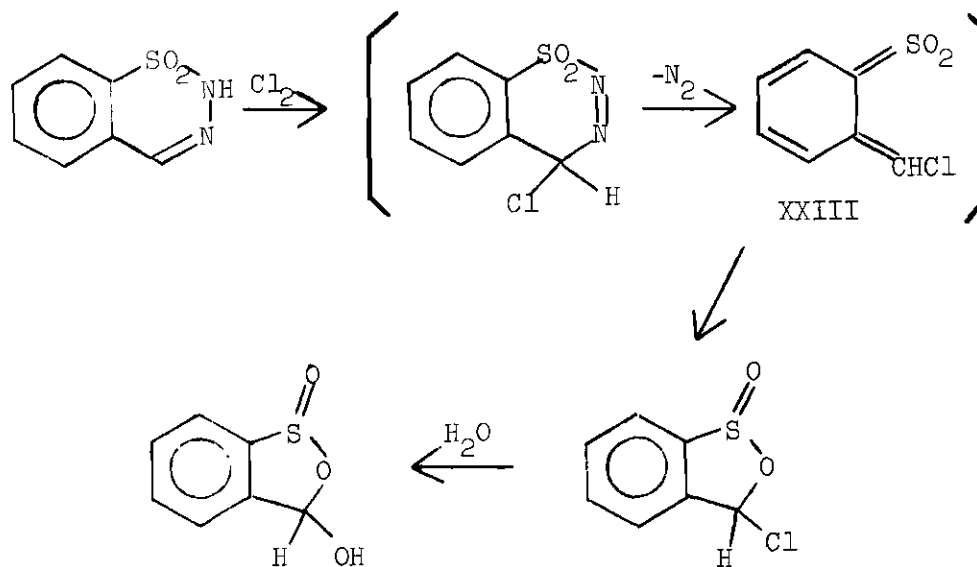
Studies of the benzo-fused thiete ring system have centered about derivatives of the stable 2H-naphth[2,3-b]thiete-1,1-dioxide (XVII) (13, 14). Rearrangement via the valence isomer XVIII, to give XIX occurs upon thermolysis (15).



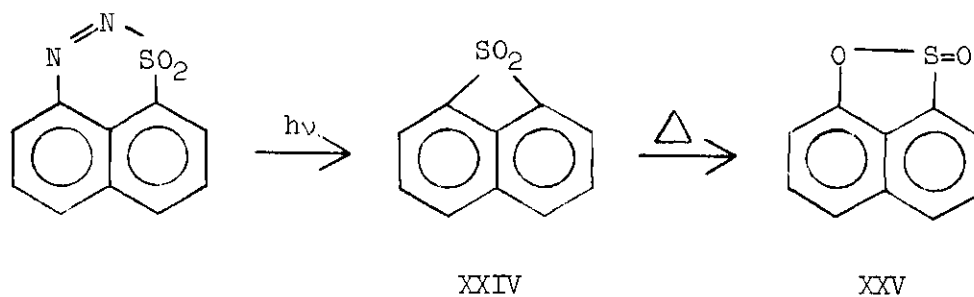
No nucleophilic or cyclo-addition reactions of XVIII have been reported, however, some studies on the reductive ring opening of XVII have appeared (14). Similar thermal rearrangements have been observed in thietes dioxides (XX).



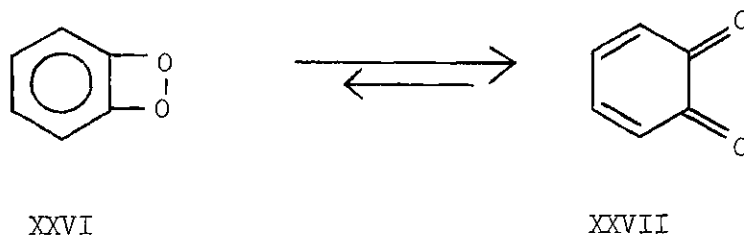
Clear evidence for the sulfene intermediate (XXI) was established by the formation of phenylallylsulfonate (XXII) when XXa was thermolized in the presence of phenol (16). Both transformations can be visualized as an electrocyclic opening of a cyclobutene-like system to give a vinylsulphene intermediate. A sulfene intermediate (XXIII) was also been proposed in the following transformation (17).



In another series a compound with a rather unique structure (XXIV) was photochemically synthesized (18) and upon thermolysis rearranged to XXV (19). A different mechanism is obviously operative in this case.



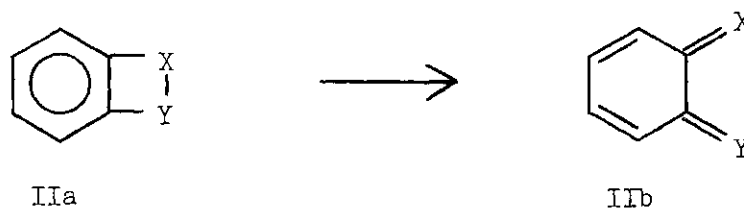
The chemistry of benzo-fused four-membered heterocycles containing two heteroatoms has not been explored. The only possible example of such a compound was described by Willstatter in 1908 (20). Colorless prisms,



assigned structure XXVI, which possessed the oxidation property of quinones and isomerized very rapidly into the ordinary, more stable red crystalline o-quinone XXVII were found when pyrocatechol was oxidized with silver oxide in ether.

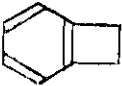
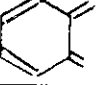
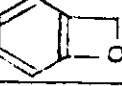
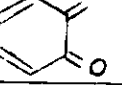
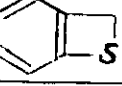
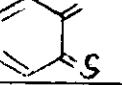
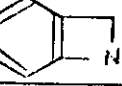
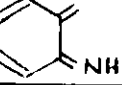
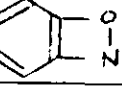
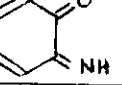
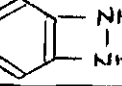
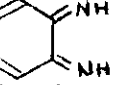
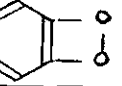
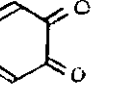
The failure of a benzothiazete synthesis by a non-photochemical route was reported recently (21).

Release of strain in systems such as IIa may be accomplished by valence tautomerization to IIb. The ease of this process is partially dependent upon the thermodynamic total energy differential as expressed in terms of bond, strain and delocalization energies (DE_{π}) of the tautomers.



In order to gain insight into the comparable stabilities of IIa vs. IIb we have constructed Table 1 which expresses the total energy (E_T) as a function of the $\sigma(E_\sigma)$ and $\pi(E_\pi)$ -electron structure (neglecting strain) for some of these heterocycles. The difference in E_σ is the energy of the bond X-Y (22). A simple Hückel calculation (23,24) provides E_π in terms of β . It is interesting to note that in general the delocalization energy per π -electron for IIa exceeds that of IIb and the stability difference between any two valence tautomers is closely a function of ΔE_σ .

Table 1. The Total Energy (E_{π}) of Some Heterocycles IIa As Function of the $\sigma(E_{\sigma})$ and $\pi(E_{\pi})$ -electron Structure.

	E_{π}	DE_{π}	ΔDE_{π}	ΔE_{σ} (Kcal./mole)
	$8\alpha + 8.000\beta$	8.000β		
	$8\alpha + 9.954\beta$	9.954β	1.954β	80.5
	$8\alpha + 8.197\beta$	8.197β		
	$8\alpha + 10.342\beta$	10.342β	2.145β	79
	$8\alpha + 8.160\beta$	8.160β		
	$8\alpha + 10.766\beta$	9.626β	1.766β	72
	$8\alpha + 11.233\beta$	8.233β		
	$8\alpha + 10.564\beta$	10.042β	1.831β	66
	$10\alpha + 15.490\beta$	8.490β		
	$8\alpha + 11.748\beta$	10.228β	1.738β	53
	$10\alpha + 17.593\beta$	8.593β		
	$8\alpha + 12.042\beta$	10.042β	1.949β	37
	$16\alpha + 16.458\beta$	8.458β		
	$8\alpha + 12.314\beta$	10.314β	1.856β	34

From consideration of this relationships one may anticipate that the most likely structures for isolation and study as representatives of IIa are the cases where $Y = SO_2$ and $X = O$ or NR . Therefore, the purpose of this research was to synthesize a 1,2,3,4-benzothiatriszine-1,1-dioxide derivative as a photochemical precursor to the theoretically significant small ring heterocycle, benzothiazete dioxide, and to subsequently study the intramolecular rearrangements and fragmentation reactions of this small ring.

CHAPTER II

EXPERIMENTAL

Apparatus and Techniques

The instruments and equipment used were described previously in Chapter II, Part I of this thesis.

ExperimentalPreparation of 2-Phenyl-2H-1,2,3,4-benzothiazine-1,1-dioxide (XXXa)

The preparation of XXXa was carried out according to the method of Ullmann (25). The colorless needles obtained had a mp 121° (dec) [lit. (25) 111° (dec)].

Irradiation of XXXa

A solution of XXXa (1.5 g, 0.0058 mole) in 250 ml of dry benzene was irradiated (Pyrex filter) at 30° for 40 min. in the photolysis apparatus described previously. During this period nitrogen was evolved very rapidly from the reaction mixture. After concentration of the benzene solution under reduced pressure at room temperature, the residue was triturated with dry n-hexane, and this solvent was evaporated under reduced pressure. Tlc (benzene) of the residue indicated at least three components were present. By fractional crystallization at -78° from hexane-benzene, carbazole (XXXV)* (0.11 g, 11.3%) and N-phenyl-o-amino sulfonic acid (XXXIIIa) (0.55 g, 38%): mp 187° (dec) were isolated.

*

XXXV was identified by comparison with an authentic sample.

For the latter an exact mass determination gave 249.042 (for $C_{12}H_{11}NO_3S$: 249.046 calculated).

In another experiment, 1 ml of dry aniline was added in the dark to the previously described reaction mixture. This reaction mixture was stirred for 1 hour to give 0.09 g (9.3%) of XXXV, and 0.42 g (22%) of N,N'-diphenyl-o-aminobenzenesulfonamide (XXXIVa): mp $171-2^\circ$; ir ($CHCl_3$) 3345 (NH), 1312, 1167 (SO_2) cm^{-1} , whose exact mass determination gave 324.092 (for $C_{18}H_{16}N_2O_2S$: 324.093 calculated).

In yet another experiment, a benzene solution of XXXa was irradiated under the same conditions for 1.5 hrs. At the end of this irradiation period a black polymer had precipitated from the reaction mixture. This polymer was removed by quick filtration and the filtrate was re-subjected to irradiation for an additional 45 min. The reaction mixture was worked up as described previously to yield 0.32 g (33%) of XXXV.

In a final experiment a solution of XXXa (1.5 g, 0.0058 mole) in 250 ml of dry toluene was irradiated (Pyrex filter) at -78° for 4 hrs. with a 450 watt Hanovia lamp. Nitrogen was evolved slowly from the reaction mixture during the photolysis period. After the reaction was complete as evidenced by cessation of nitrogen evolution, the resulting solution was cautiously transferred under dry nitrogen into a flask and the solvent was removed under reduced pressure at room temperature. A dark brown solid residue was obtained which was triturated with hexane-benzene mixtures. Concentration of the filtrate under reduced pressure gave a brown powdery residue which resisted crystallization from hexane-benzene at -78° . On standing at room temperature, the color of the residue became purple and there resulted a compound which was

identified by tlc (benzene) as XXXIIIIa.

Thermolysis of XXXIa

One gram (0.0039 mole) of XXXa was irradiated (Pyrex filter) at -78° in 250 ml of dry *p*-xylene. After 3.5 hrs. when tlc (benzene) showed the starting material had disappeared, the resulting solution was transferred without exposure to the atmosphere into a flask and the solution heated in an oil bath at 130° under dry nitrogen for 20 min. Removal of the solvent in vacuo gave a solid residue which was triturated with benzene to yield crude phenothiazine-5,5-dioxide (XXXVIa) 0.26 g (29%) identified by comparison with an authentic sample after crystallization from ethanol (26,27). Compound XXXIIIIa also was present in the residue as minor product.

Thermolysis of XXXa

One gram (0.0039 mole) of XXXa in 250 ml of dry *p*-xylene was heated under a dry nitrogen atmosphere at 130° for 10 min. Nitrogen was rapidly evolved from the reaction mixture. Solvent was removed in vacuo and the residue was crystallized from ethanol to afford 0.35 g (36%) of pure XXXVIa.

Irradiation of XXXVIa

A solution of 0.5 g (0.0022 mole) in 250 ml of dry benzene was irradiated at 30° for 3.5 hrs. in the same manner as described previously. Tlc (10% ethanol in benzene) indicated no reaction and only starting material was recovered.

Preparation of N-(*t*-Butyl)-*o*-nitrobenzenesulphonamide (Lb)

To 15 g (0.2 mole) of *t*-butylamine was added dropwise at 0° a solution of 22 g (0.1 mole) of *o*-nitrobenzenesulphonyl chloride in

100 ml of ethanol. After the addition was complete the reaction mixture was warmed on a steam bath for 20 min. and then cooled in an ice bath. The crude product which precipitated was collected and recrystallized from ethanol to give 25 g (99%) of Ib as colorless needles: mp $142-2^{\circ}$; nmr (CDCl_3) τ 1.66-2.39 (m, 4H), τ 4.71 (broad, 1H), τ 8.68 (s, 9H).

Preparation of N-(t-Butyl)-o-aminobenzenesulphonamide (Llb)

To a hot solution of stannous chloride (68 g, 0.3 mole) in 140 ml ethanol was slowly added 25 g (0.1 mole) of Ib. When the addition was complete, concentrated hydrochloric acid (68 ml) was then carefully added and the reaction mixture allowed to stand for 10 min. After the removal of the solvent under reduced pressure, the residue was treated with dilute aqueous sodium hydroxide until pH 2 was reached and the crude product which precipitated was collected and crystallized from ethanol to yield 17 g (62%) of colorless needles of Llb: mp $114-5^{\circ}$; nmr (CDCl_3) τ 2.17-3.46 (m, 4H), τ 5.03 (broad, 2H), τ 5.37 (broad, 1H), τ 8.80 (s, 9H).

Preparation of Triazine XXXb

A solution of 8 g (0.035 mole) of Llb, 80 ml of water, 25 ml of concentrated hydrochloric acid and 10 ml of ethanol was cooled in an ice bath to 0° . To this solution was added in one portion with stirring 2.5 g (0.04 mole) of sodium nitrite in 5 ml of water. After stirring at 0° for 10 min. the reaction mixture was neutralized with a saturated aqueous solution of sodium acetate. The crude produce which precipitated was collected and crystallized from ethanol to give 7.5 g (90%) of colorless needle of XXXb: mp $85-6^{\circ}$; nmr (CDCl_3) τ 1.83-2.36 (m, 4H), τ 8.19 (s, 9H); ir (CHCl_3) 1436 (N=N), 1335 , 1160 (30_2) cm^{-1} ; the mass spectrum

showed a molecular ion at m/e 239.

Irradiation of XXXb

Triazine XXXb (1.5 g, 0.0063 mole) in dry benzene (250 ml) was irradiated for 3 hrs. at 30° . Nitrogen evolved slowly from the reaction mixture during this period. The reaction mixture was separated into its components by trituration with benzene-hexane as described previously. Isolated was a large amount of brown polymer and 0.22 g (17%) of t-butylbenzenesulphonamide (XLIIb): mp $135-8^\circ$; nmr ($CDCl_3$) τ 2.22-3.19 (m, 5H), τ 7.70 (broad, 1H), τ 8.81 (s, 9H); ir ($CHCl_3$) 3242 (NH), 1131, 1145 (SO_2) cm^{-1} ; the mass spectrum showed a molecular ion at m/e 213.

In another experiment, XXXb (1.5 g, 0.0063 mole) in dry THF (250 ml) was irradiated at $-78^\circ C$ for 8 hrs. Nitrogen slowly evolved during this period. Purification afforded 0.30 g (21%) of XLIIb.

In still an another experiment, XXXb (1 g, 0.0042 mole) in 250 ml of dry benzene and 1 ml of dry aniline was irradiated for 8 hrs. at $30^\circ C$. After the solvent was evaporated, the residue was fractionated as described above to yield 0.28 g (22%) of o-anilinobenzenesulphon-t-butylamide (XLII): mp $174-6^\circ$; nmr ($CDCl_3$) τ 1.86-2.98 (m, 9H), τ 7.08 (broad, 1H), τ 7.38 (broad, 1H), τ 8.81 (s, 9H); ir ($CHCl_3$) 3278, 3200 (NH) 1315, 1145 (SO_2) cm^{-1} ; the mass spectrum showed a molecular ion at m/e 304.

Thermolysis of XXXb

Triazine XXXb (1 g, 0.042 mole) in dry p-xylene was heated in an oil bath at 138° under a nitrogen atmosphere for 10 hrs. After evaporation of solvent, the residue was dissolved in a minimum amount of benzene and then treated with hexane to precipitate the brown polymer. The polymer was removed by filtration, the filtrate was concentrated

and placed in the freezer overnight. The solid product which crystallized was identified as XLIIb by mixture melting point with an authentic sample.

Preparation of *o*-Nitrobenzenesulphon-2,6-dimethylanilide (Lc)

To a solution of 2,6-dimethylaniline (13.2 g, 0.11 mole) in pyridine (10 ml) was slowly added 22 g (0.1 mole) of *o*-nitrobenzenesulphonyl chloride with stirring at 0°. After the addition was complete, the reaction mixture was treated with warm ethanol from which crude product crystallized on cooling. After recrystallization twice from ethanol 18 g (60%) of pure Lc was obtained as colorless needles: mp 164-5°; nmr (CDCl₃) τ 1.93-3.00 (m, 7H), τ 7.50 (broad, 1H) τ 7.86 (s, 6H).

Preparation of *o*-Aminobenzenesulphon-2,6-dimethylanilide (LIc)

To a warm ethanolic (84 ml) solution of stannous chloride (42 g, 0.185 mole) was added 18 g (0.06 mole) of Lc over 10 min. As soon as this addition was complete concentrated hydrochloric acid (42 ml) was cautiously added to the reaction mixture. The crude hydrochloride salt of LIc which crystallized from the solution when cooled was collected and dissolved in 200 ml of dilute sodium hydroxide. Upon neutralization with acetic acid of this solution, the crude free base precipitated and was collected. Recrystallization from ethanol-water yielded 13.6 g (84%) of pure crystalline LIc: mp 143-5°; nmr (CDCl₃) τ 1.94-3.10 (m, 7H) τ 7.45 (broad, 1H), τ 7.15 (broad, 2H) τ 7.86 (s, 6H).

Preparation of Triazine XXXc

To a 10% aqueous solution of hydrochloric acid (75 ml) was added dropwise with stirring at 0° a cold solution containing LIc (5.3 g,

0.019 mole), sodium hydroxide (4.0 g) and sodium nitrite (1.4 g, 0.02 mole) in 50 ml of water. After the addition was complete, the reaction mixture was allowed to stir at 0° for an additional 15 min. The yellow precipitate formed was quickly collected and discarded and the filtrate neutralized with aqueous saturated sodium acetate. The crude XXXc which precipitated was collected and recrystallized from ethanol to give 4.4 g (80%) of colorless needles of XXXc: mp 151° (dec); nmr (CDCl₃) τ 1.78-2.83 (m, 7H), τ 7.68 (s, 6H); ir (CHCl₃) 1442 (N=N), 1345, 1159 (SO₂) cm⁻¹; the mass spectrum showed a molecular ion at m/e 287.

2-(2,6-Dimethylphenyl)-benzothiazete-1,1-dioxide (XXXIc)

In a photolysis apparatus 1 g (0.0035 mole) of the triazine XXXc in 250 ml of dry benzene was irradiated (Pyrex filter) at 30° for 1.5 hrs. Nitrogen evolved slowly from the solution during this period. After the irradiation was complete the reaction mixture was carefully transferred to a flask without exposure it to the atmosphere.* Removal of the solvent in vacuo gave a brown solid residue which was dissolved in a minimum amount (5 ml) of dry benzene and then was treated with hexane to precipitate a brown polymer. The filtrate obtained was concentrated under reduced pressure and retreated with hexane to precipitate the last trace of polymer. After cooling the concentrated filtrate, pure XXXIc (0.55 g, 61%) crystallized as prisms: mp 112-3° (dec); nmr (CDCl₃) τ 1.88-3.47 (m, 7H), τ 7.68 (s, 6H); ir (CHCl₃) strong absorption at 1345 and 1160 (SO₂) cm⁻¹. Exact mass determination gave 259.066 (for C₁₄H₁₃NO₂S: 259.067 calculated).

*

During the entire work-up process caution was exercised to avoid contact with atmospheric moisture.

The benzothiazete XXXIc when exposed to the air for few hours slowly changed color (purple). This transformation product was identified as o-(2,6-dimethylphenyl)aminobenzenesulfonic acid (XXXIIIc) which had mp 163-5° (dec) and exact mass determination gave 277.073 (for $C_{14}H_{15}NO_3S$: 277.077 calculated).

(a) Reaction with Aniline: The benzothiazete XXXIc (0.5 g, 0.0019 mole) was stirred overnight at room temperature with dry aniline (2 ml). After evaporation of excess aniline in vacuo, the residue was taken up in dry benzene (2 ml) and then treated with hexane to precipitate insoluble impurities. After filtration, the filtrate was concentrated in vacuo and cooled. Pure o-(2,6-dimethylanilino)-benzenesulphonanilide (XXXIVc) (0.19 g, 29%) crystallized from the cold filtrate as colorless needles mp 100-102°. Exact mass determination gave 352.123 (for $C_{20}H_{20}N_2O_2S$: 352.125 calculated).

(b) Reaction with Norbornene: The benzothiazete XXXIc (0.5 g, 0.0019 mole) and norbornene (2 g, 0.021 mole) was refluxed for 6 hrs. The excess norbornene was evaporated in vacuo and the residue of the crude exo-XXXIc-norbornene adduct was recrystallization from ethanol afforded 0.2 g (32%) of crystalline XXXVIII: mp 173-4°, nmr ($CDCl_3$) τ 2.00-3.37 (m, 8H), τ 3.74 [m, 1H(C_2), $W_{\frac{1}{2}}^*$ 2.5 Hz] τ 6.72 (m, 1H), τ 6.88 (m, 1H), τ 7.83 (s, 6H), τ 8.00-9.00 (m, 6H). Exact mass determination gave 353.147 (for $C_{21}H_{23}NO_2S$: 353.145 calculated).

(c) Pyrolysis of XXXIc: The benzothiazete XXXIc (0.5 g, 0.0019 mole) in dry toluene (20 ml) was refluxed for 3 hrs. After removed of the solvent under reduced pressure, the residue was treated with benzene

* $W_{\frac{1}{2}}$ is half-height width of C_2 -H signal.

and hexane to remove the polymer. A crude product crystallized from the cold filtrate which was collected and recrystallized from ethanol to give 0.06 g (11%) of bright yellow needles of 1,4a-dimethyl-4aH-phenothiazine-5,5-dioxide (XXXVIc): mp $83-4^{\circ}$; ir (CHCl_3) 1305, 1150 (SO_2) cm^{-1} ; nmr (CDCl_3) τ 2.00-2.76 (m, 4H), τ 3.41-3.78 (m, 3H) τ 7.93 (s, 3H) τ 8.40 (s, 3H). Exact mass determination gave 259.066 (for $\text{C}_{14}\text{H}_{13}\text{NO}_2\text{S}$: 259.067 calculated).

(d) Irradiation of XXXIc: A solution of the benzothiazete XXXIc in 250 ml of dry hexane was irradiated (Quartz) at 30° for 3.5 hrs. No monomeric compounds could be isolated from this photolysate.

Thermolysis of XXXc

The triazine XXXc (1 g, 0.0035 mole) in dry mesitylene (25 ml) was heated to 150° in an oil bath for 45 min. under a dry nitrogen atmosphere. Nitrogen evolved from the reaction during this period. After evaporation of the solvent in vacuo, the residue after crystallization from ethanol gave 0.23 g (25%) of yellow crystalline XXXVIc. Tlc (benzene) indicated a trace of the benzothiazete XXXIc also present in this residue.

Preparation of o-Nitrobenzenesulphonhydrazide (XXVIII)

Compound XXVIII was prepared according to the method of Gremly (28). The yellow crystalline hydrazide had a mp 101° (dec) [lit. (28) 101° (dec)].

Preparation of Benzophenone-o-Nitrobenzenesulphonhydrazone (Id)

To a solution of benzophenone (6.7 g, 0.037 mole) in absolute ethanol (50 ml) was added a 5 drops of acetic acid and 8 g (0.037 mole) of XXVIII. The crude product crystallized from the solution after

heating the reaction mixture on a steam bath for 40 min. followed by cooling in an ice bath. The hydrazone was collected by filtration and crystallized from ethanol to give 4.3 g (31%) of pure Id as colorless needles: mp 160-1°, the mass spectrum showed a molecular ion at m/e 381.

Preparation of Benzophenone-O-Aminobenzenesulphonhydrazone (LIId)

A solution of Id (4.3 g, 0.011 mole), 150 ml of THF and 15 ml of water was stirred with 3 g of aluminum amalgam at 5° for 2 hrs. (29). The reaction mixture was then filtered through a Celite bed and the filtrate was evaporated under reduced pressure. The residue was then crystallized from ethanol to afford crude LIId. Recrystallization from ethanol gave 3.0 (76%) of pure LIId as pale yellow needles: mp 84-5° nmr (CDCl₃) τ 2.27-2.81 (m, 15H) τ 4.18 (s, 2H).

Preparation of 2-Benzhydrylideneamino-2H-1,2,3,4-benzothiazine-1,1-dioxide (XXXd)

To a solution of LIId (2 g, 0.0057 mole) in 50 ml of glacial acetic acid was added an aqueous saturated solution of sodium nitrite (3 g, 0.045 mole) at 5° with stirring. After stirring for 10 min. the reaction mixture was diluted with cold water and the yellow precipitate which formed was collected and recrystallized from benzene-hexane at -78° to yield 1.5 g (73%) of pure XXXd: mp 57-9° (dec); ir (CHCl₃) 1491 (C=N), 1434 (N=N) 1323, 1140 (SO₂) cm⁻¹; the mass spectrum showed a molecular ion at m/e 362.

3-Benzhydrylideneamino-3H-2,1,3-benzoxathiazole (XLIIId)

The triazine XXXd (3 g, 0.0083 mole) was irradiated in 250 ml of dry benzene at 30°. Initially nitrogen was evolved rapidly from the reaction mixture but after 1 hr. evolution of nitrogen ceased. The

solvent was evaporated under reduced pressure and the residue was taken up in benzene-hexane. After cooling to -78° a fine white crystalline precipitate formed which was collected and recrystallized from ethanol to afford 0.84 g (40%) of pure colorless needles of XLIIId: mp $198-200^{\circ}$; ir (CHCl_3) 1492 (C=N), 1030 (S-O) cm^{-1} . Exact mass determination gave 334.074 (for $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$: 334.078 calculated). The filtrate was chromatographed over florisil and elution with benzene gave 0.8 g (27%) of the starting triazine XXXd.

Thermolysis of XXXd

The triazine XXXd (1 g, 0.0028 mole) in benzene (25 ml) was refluxed under dry nitrogen for 1 hr. After removed of the solvent in vacuo, the residue was purified as described above and the colorless product obtained was recrystallization from ethanol to yield 0.2 g (22%) of 6-phenyl-dibenzo[b,g]-4H-1,4,5-thiadiazocine (XLIII): mp $160-1^{\circ}$; nmr (CDCl_3) τ 1.75-2.88 (m, 14H) τ 3.55 (broad, 1H*); mass spectrum $M^+(\text{m/e})$ 334. Tlc (benzene) indicated a trace of the benzoxathiazole XLIIId was also present in the residue.

In another experiment the triazine XXXd (1 g, 0.0028 mole) was refluxed in 25 ml of dry acetonitrile for 1 hr. and the product was purified as described above to give 0.25 g (27%) of XLIIId. Tlc (benzene) indicated a trace of XLIII was present in the reaction mixture.

Thermolysis of the Benzoxathiazole XLIIId

A solution of XLIIId (0.1 g, 0.003 mole) and 5 ml of dry benzene was passed dropwise through a vertical tube (11 x 0.8 cm, packed with helices) heated to 250° under a nitrogen stream and purification of

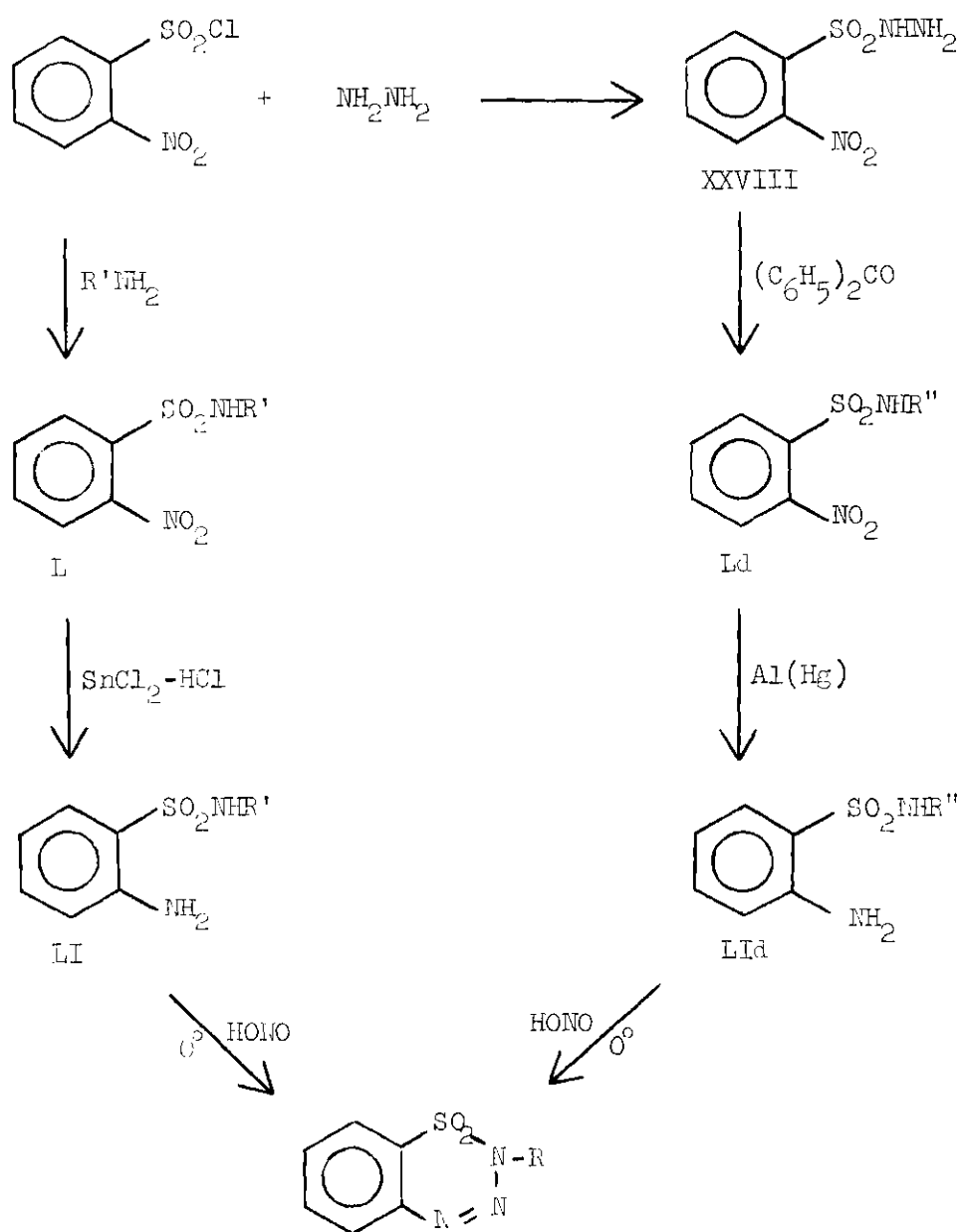
* Estimated.

the polyolcate by the procedure described above yielded 0.015 g (15%) of XLIII.

CHAPTER III

DISCUSSION OF RESULTS

The precursor triazines XXXa, XXXb, XXXc and XXXd employed in this investigation were prepared in moderate to high yield according to the following synthetic sequence.

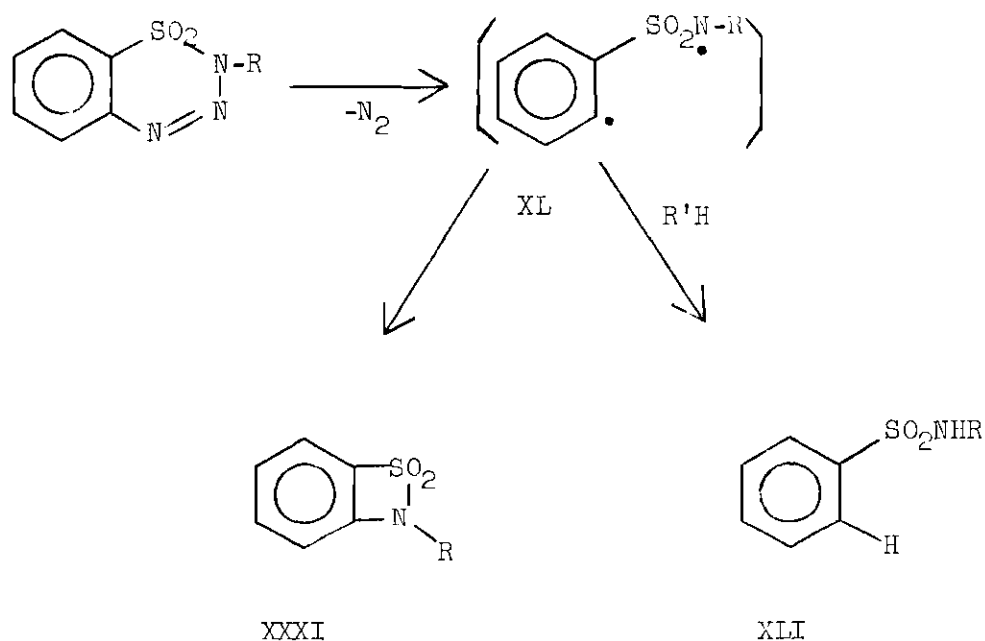


- a. $R = R' = Ph$
 b. $R = R' = tBu$
 c. $R = R' = 2,6\text{-dimethylphenyl}$
 d. $R = R'' = -N=C(C_6H_5)_2$

XXX

Chart I. Synthetic Route to Compounds XXXa, XXXb, XXXc, XXXd

Spectroscopic data obtained for these compounds are consistent with the assigned structures. All of the prepared triazines readily underwent photolytic or thermal loss of nitrogen with formation of the 1,4-diradical intermediate XL which subsequently underwent cyclization to XXXI or radical hydrogen abstraction from solvent to give XLI depending on the substituent R.



Irradiation (3000 Å) of XXXs in benzene at 30° or in toluene at -78° resulted in a rapid evolution of nitrogen and provided a crude solid which resisted purification due to its thermal instability. Clear evidence of the existence of XXXIa in this photolysate was demonstrated by the following experiments. The crude photolysate reacted with added nucleophiles such as water or aniline to give the conjugate

addition products XXXIIIa or XXXIVa respectively. A mechanism which accounts for the formation of these products depends upon direct nucleophilic attack on the sulfur atom of either XXXIa or the valence isomer XXXIIa.

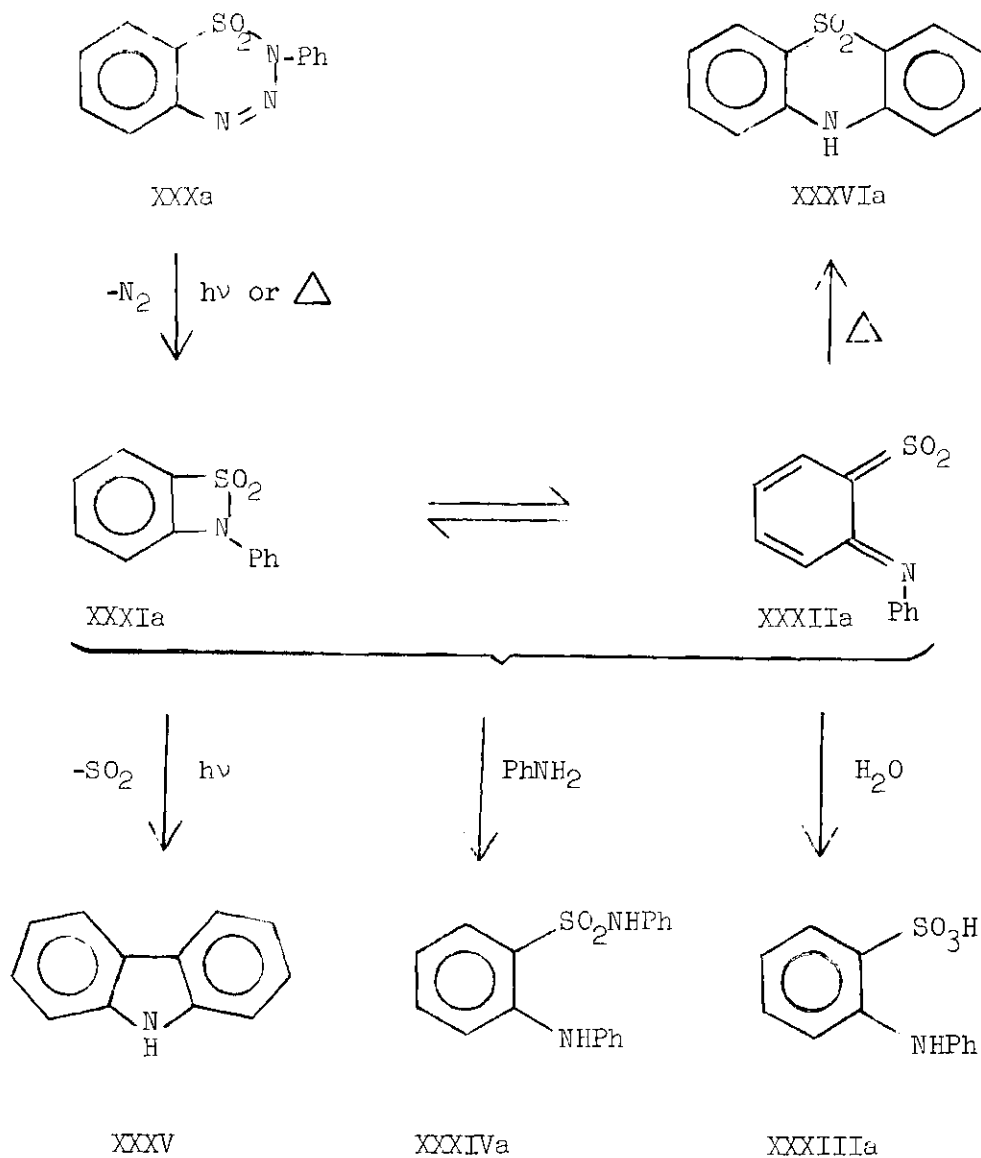


Chart II. Photochemical or Thermal Decomposition of the Triazine XXXa

Continued irradiation of XXXa slowly afforded carbazole (XXXV) and the yield of XXXV was proportional to the length of the irradiation time. The formation of XXXV is best rationalized (Chart III) by assuming the intervention of 1,3-diradical intermediate XXXVII generated by extrusion of sulfur dioxide from benzothiazete XXXIa, and whose syn-isomer subsequently cyclizes to XXXV. The same diradical intermediate has previously been invoked in the formation of carbazole from 1-phenylbenzotriazole (30). Since phenothiazine dioxide (XXXVIa) did not photochemically decompose to XXXV the possibility of its being precursor of the carbazole can be excluded from consideration.

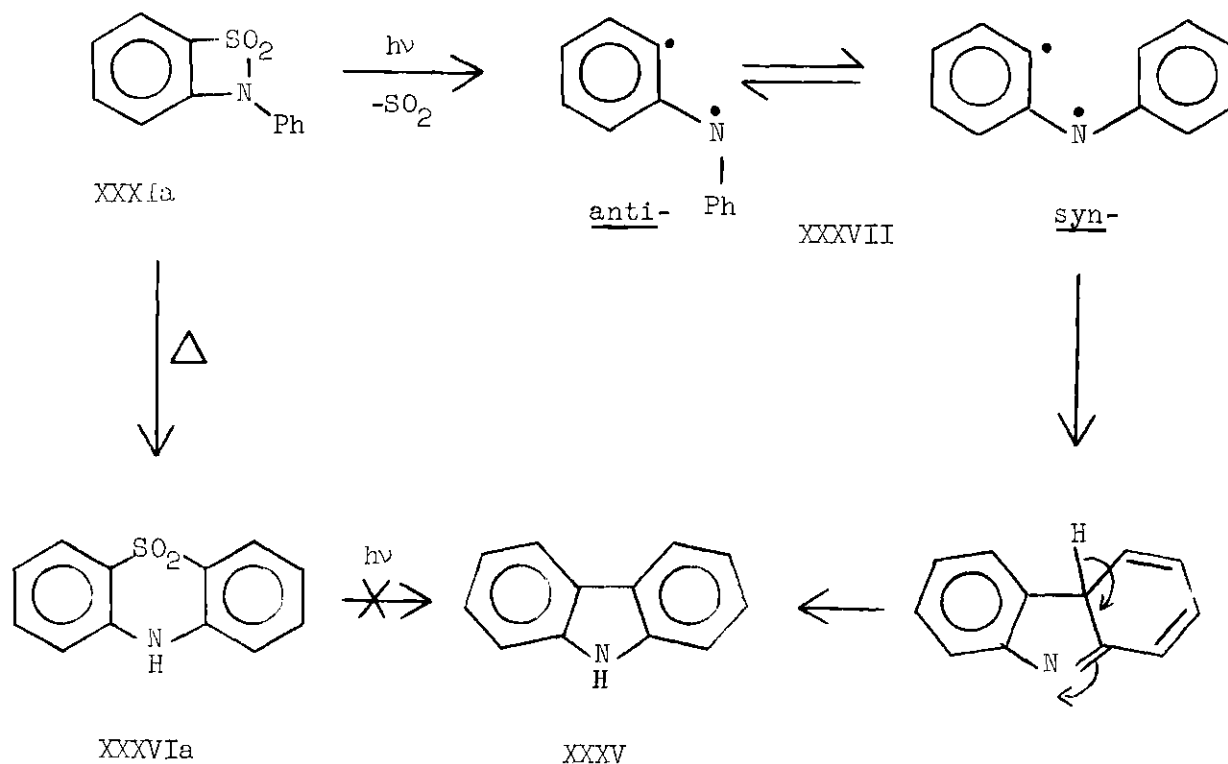


Chart III. Mechanism of Formation of Carbazole (XXXV)

In contrast with the above photolysis, thermolysis of the benzo-thiazete XXXIa gave exclusively the rearranged product XXXVIa and no trace of XXXV was detected. This rearrangement may be pictured (Chart IV) as occurring via the valence isomer XXXIIa which undergoes intramolecular cyclization ($2\pi + 4\pi$) followed by aromatization to give XXXVIa. A similar rearrangement has been proposed in the photolysis of 3-phenyl-benzotriazone XIIIa (11).

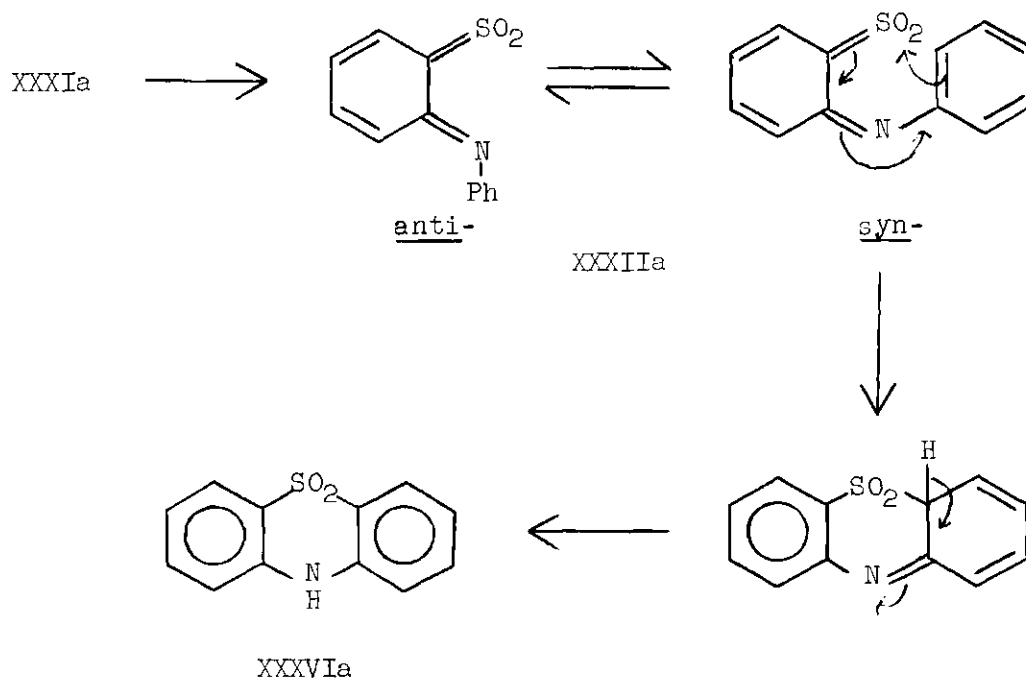


Chart IV. Mechanism of Phenothiazine Dioxide (XXXVIa) Formation

Thermolysis of the triazine XXXa in *p*-xylene at 130° also gave XXXVIa. The generation of XXXIa must be the initial step leading toward the observed products. In order to make the isomerization of XXXI to

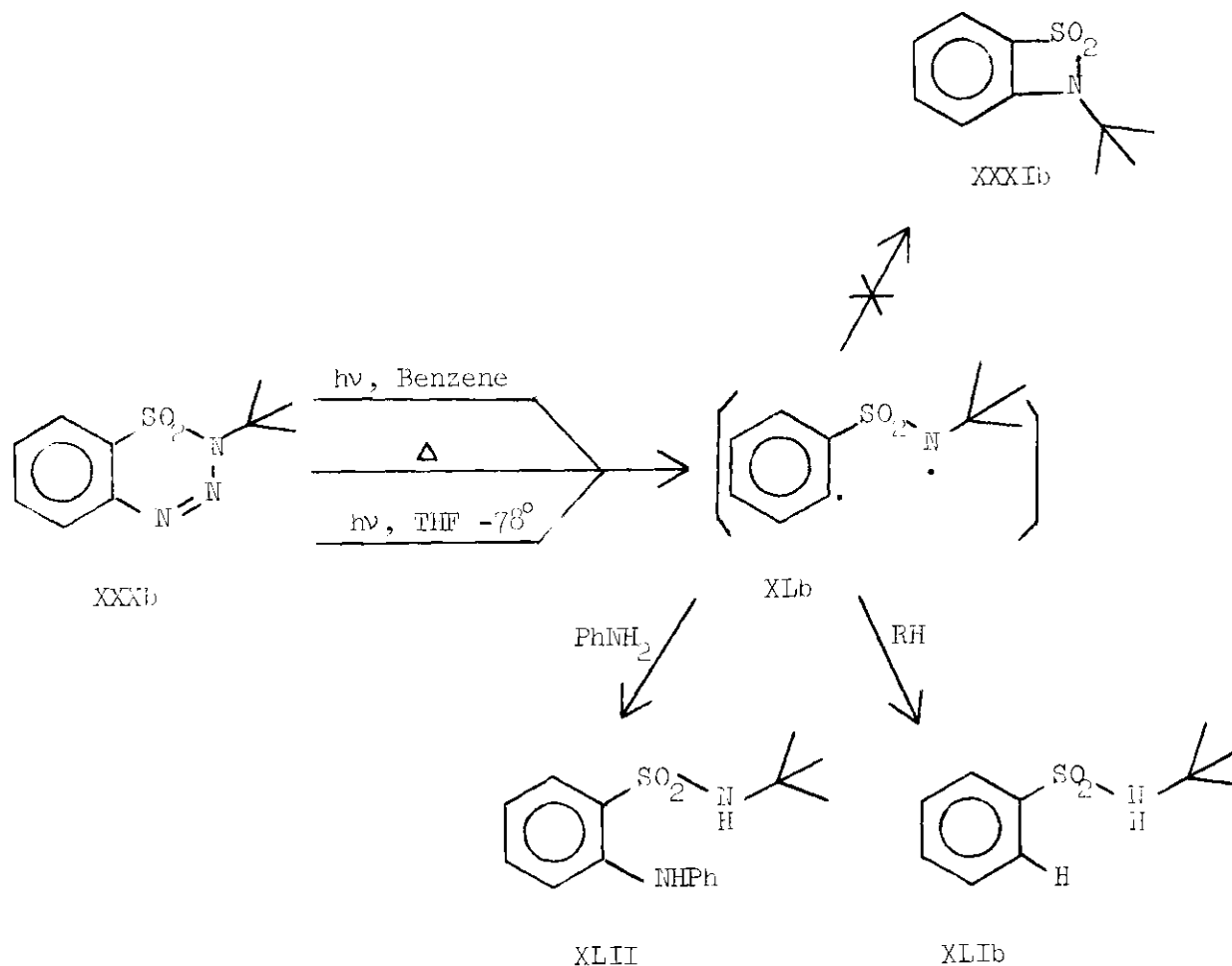


Chart V. Photochemical or Thermal Decomposition of the Triazine XXXb

This suggests that because of the lack of suitable phenyl conjugation the 1,4-diradical intermediate XLb was so reactive that a process of radical hydrogen abstraction was kinetically more favorable than ring closure.

From previous cases it was concluded that phenyl conjugation seems essential for the occurrence of ring closure from such 1,4-diradical

intermediates. As an alternative to the t-butyl group in order to stabilize structure XXXI bulky ortho-substituent on the phenyl group may also reduce the conjugative stability of valence isomer XXXII relative to XXXI. This would result from a twisting about the C-N bond due to a ortho-ortho steric interaction, thus destroying the coplanarity of the π -electron system in XXXII. Such a 2,6-dimethylphenyl derivative of XXXI (XXXIc) should therefore be thermally more stable than a simple phenyl derivative and incapable of carbazole formation photochemically. The prediction proved to be correct as indicated by the following results:

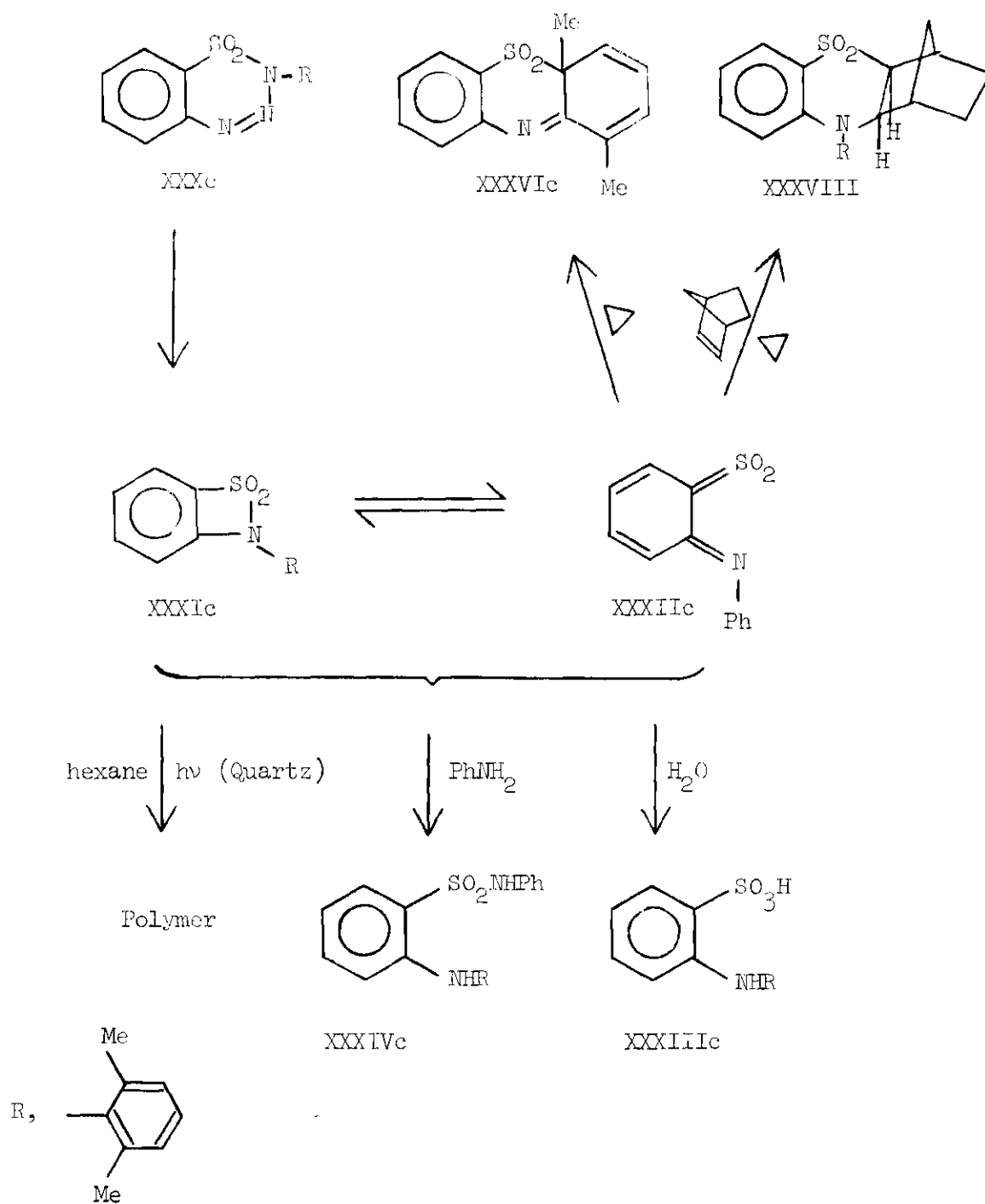
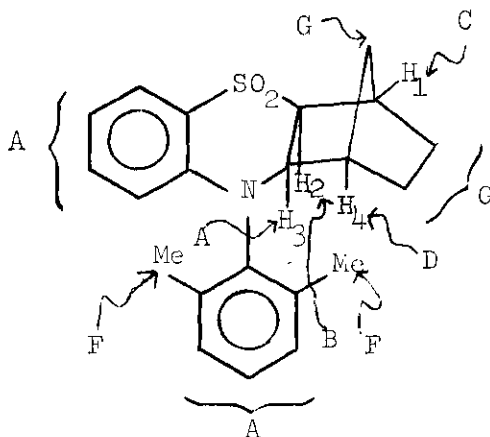


Chart VI. Photochemical or Thermal Decomposition of the Triazine XXXc

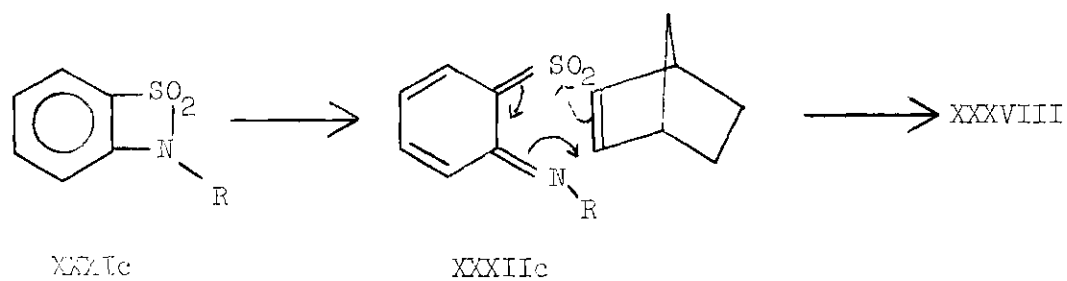
The starting triazine XXXc although more stable to photolysis than XXXa, in fact, provided a clean photolysate from which prisms of XXXIc were isolated in a yield of 61%. The reactivity toward nucleophiles of XXXIc paralleled XXXIa and spectral data were consistent with the assigned structure. The infrared spectrum showed strong sulfone absorption at 1345 and 1160 cm^{-1} . The nmr showed resonances for aromatic protons [multiplet (7H) at τ 1.88-3.47] and two equivalent methyl groups [singlet (6H) at τ 7.68]. The mass spectrum had a strong molecular ion at m/e 259 and a fragmentation ion appeared at m/e 195 ($M-\text{SO}_2$)⁺. The theoretical exact mass for a molecule $\text{C}_{14}\text{H}_{13}\text{NO}_2\text{S}$ was 259.067 as compared to the experimentally determined value of 259.066.

Reaction of XXXIc with norbornene resulted in the expected stereospecific formation exo-adduct XXXVIII. The assigned exo-structure is based on a nmr spectrum in which a 2.5 Hz ($J_{1,2}$) half-height width ($W_{1/2}$) of the H_2 signal indicates an endo-proton was coupled with the bridge-proton and therefore the exo-structure was assigned to XXXVIII (31).

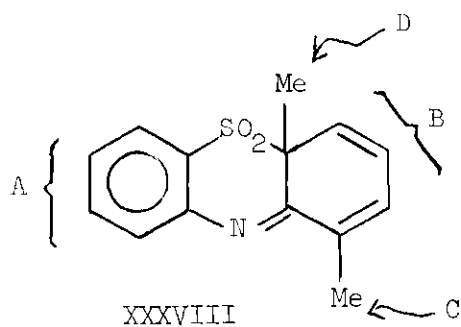


H	τ	mult. (J)
A	2.00-3.37	m
B	3.74	m ($W_{1/2}=2.5$ Hz)
C	6.72	m
D	6.88	m
F	7.83	s
G	8.00-9.00	m

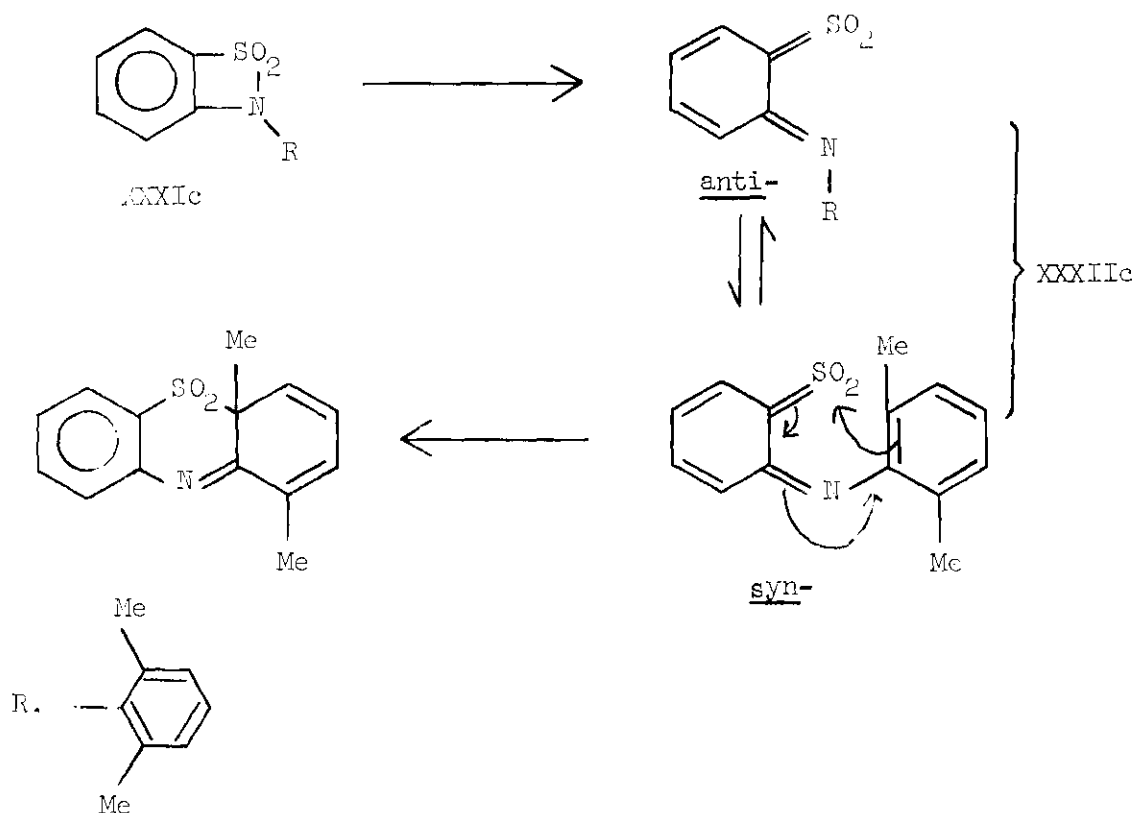
The occurrence of valence isomerization leading to XXXIIc, is further substantiated by the cycloaddition of norbornene to XXXIc. The Diels-Alder [$4\pi + 2\pi$] process proceeds via the valence isomer XXXIIc which acts as a cisoid diene system.



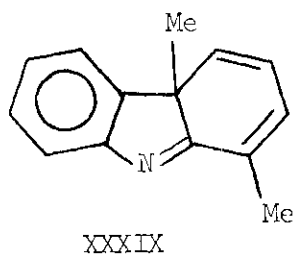
A rather novel product XXXVIc was obtained when XXXIc was heated in toluene. The nmr spectrum of this product was consistent with the assigned structure and its genesis may result from the following mechanism:



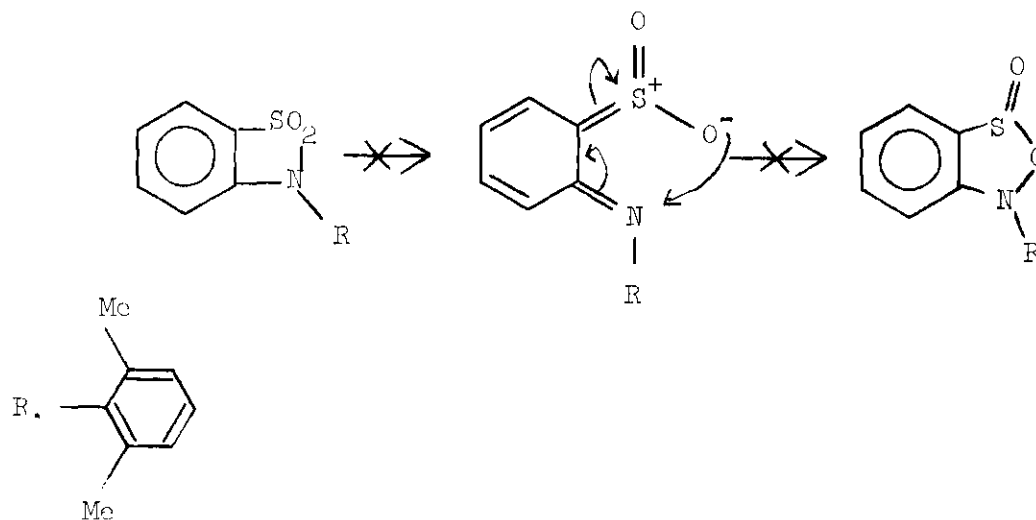
H	τ	mult.
A	2.00-2.76	m
B	3.41-3.78	m
C	7.93	s
D	8.40	s



In contrast with XXXIa, photolysis (quartz probe) of XXXIc in hexane did not afford the carbazole derivative XXXIX.



A mechanistically possible compound XLIIc which might have resulted during the formation of XXXVIc from the thermolysis of XXXIc or triazine XXXc was not obtained.



In another series, irradiation of the precursor triazine XXXd at 30° resulted in rapid evolution of one equivalent of nitrogen to provide a clean photolysate from which crystalline XLIIId was isolated in 40% yield.

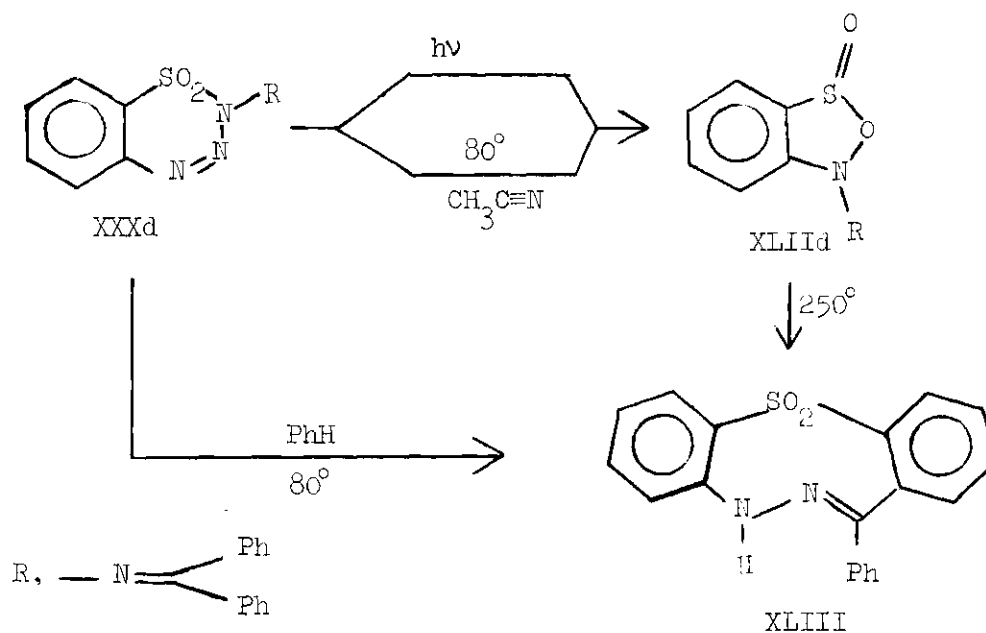
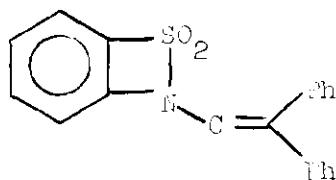
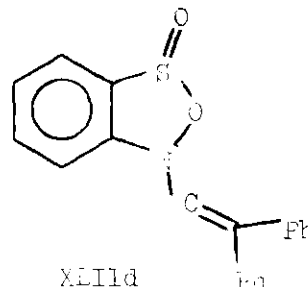


Chart VII. Photochemical or Thermal Decomposition of the Triazine XXXd

The thermal and photolytic stability found for this compound immediately excluded the four membered ring structure XXXId from consideration. The more stable benzoxathiazole structure XLIIId



XXXId



XLIIId

is proposed on the basis of the following spectral data. The infrared spectrum showed absorption at 1492 (C=N) and 1030 (SO) cm^{-1} and the mass spectrum showed a molecular ion at m/e 334 and base peak at m/e 181 which corresponds to a $(\text{Ph}_2\text{C}=\text{N})^+$ ion. The theoretical exact mass for molecule $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ was 334.078 as compare to the experimentally determined value of 334.074. The formation of the benzoxathiazole XLIIId is rationalized by assuming initial generation of XXXId which then rearranges to XLIIId at room temperature via valence isomer XXXIIId. Similar rearrangements have many precedents in benzothiete chemistry (15,16).

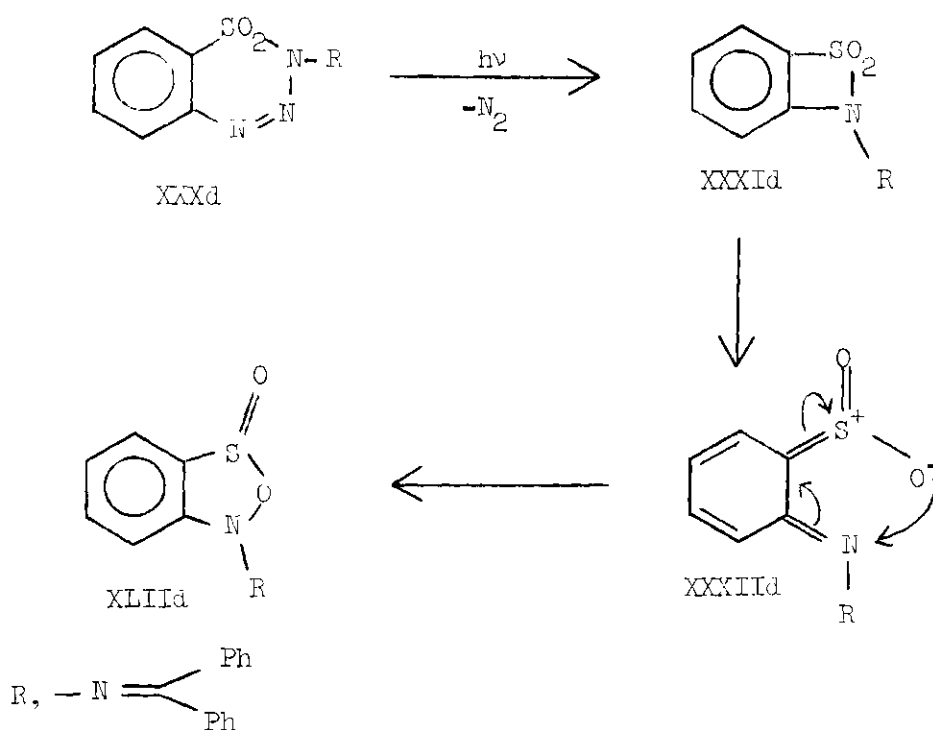


Chart VIII. Mechanism of Photochemical Formation of XLIIId

Thermolysis of XXXd in a polar solvent such as acetonitrile also yields exclusively XLIIId. On the other hand thermolysis of XXXd in a non-polar solvent such as benzene resulted in a different crystalline product which was identified as 6-phenyl-dibenzo[b,g]-4H-1,4,5-thiadiazocine (XLIII) on the basis of spectral data. The nmr spectrum showed absorptions for aromatic protons [multiplet (14H) at τ 1.74-2.88 and one amino proton [broad (1H) at τ 3.55]. The mass spectrum showed a molecular ion at m/e 334. This product (XLIII) was also isolated in low yield from the pyrolysis of the benzoxathiazole XLIIId at 250°. These

isomerizations may be visualized as occurring via the following mechanism.

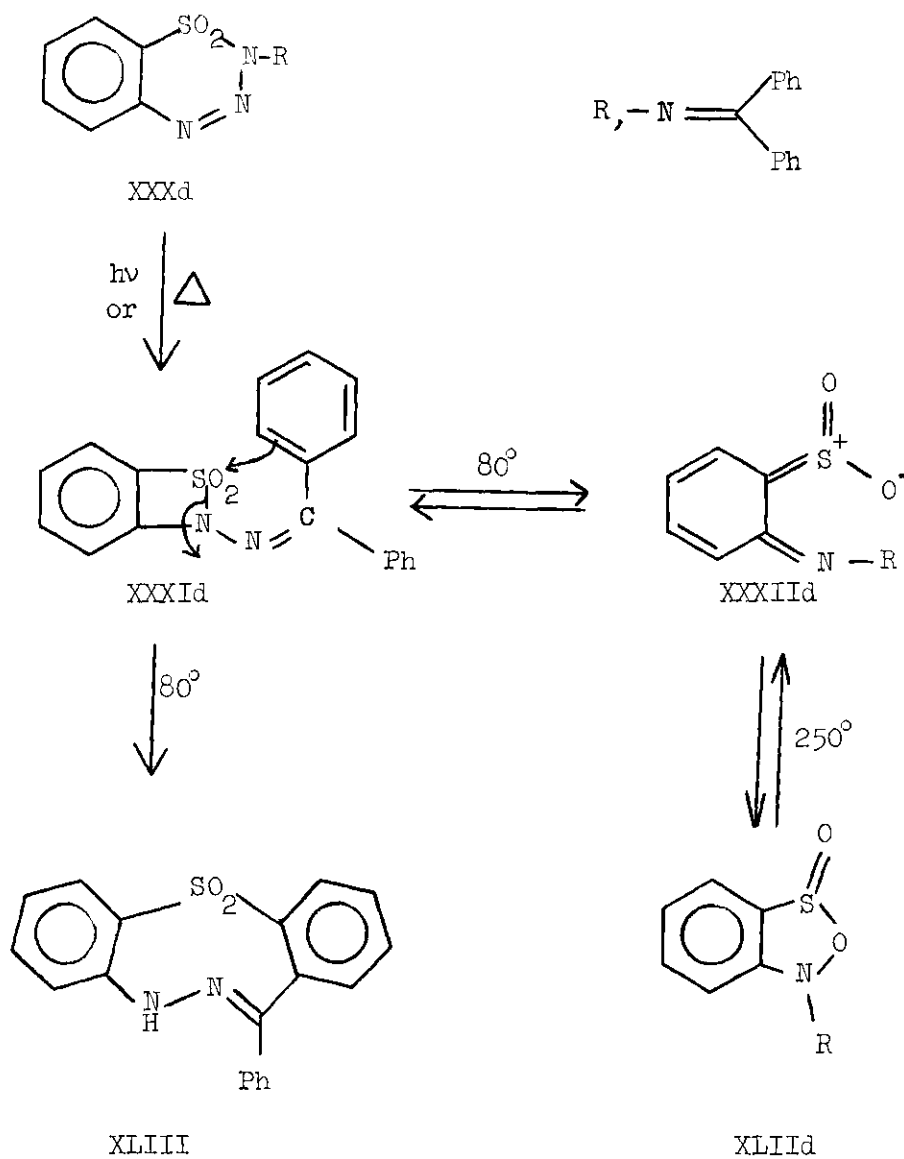


Chart IX. Mechanism of Thermal Formation of XLIIId and XLIIId

Thermolysis of XXXd initially generated XXXId which then isomerized either to XXXIId and then to XLIId or via a ring-opening process (through a six-membered transition state) to XLIII depending on the polarity of the solvent. The former process was facilitated in a polar solvent (acetonitrile) while the latter proceeded in a non-polar solvent (benzene). Thermolysis of XLIId at 250° to give XLIII may occur through the intermediate formation of XXXIId and XXXId.

CHAPTER IV

CONCLUSIONS

A new heterocycle, benzo-fused four membered ring containing two heteroatoms XXXI has been photolytically synthesized from precursor substituted 2H-1,2,3,4-benzothiatriazine-1,1-dioxides XXX.

2-(2,6-Dimethylphenyl)-2H-benzothiazete-1,1-dioxide (XXXIc) was isolated and found to be thermally stable, and reacted readily with nucleophiles, and underwent expected thermal rearrangements.

Although 2-phenyl-2H-benzothiazete-1,1-dioxide (XXXIa) was not thermally stable enough to permit isolation; its existence in the photolysate of triazine XXXa was confirmed by its similar reactivity toward nucleophiles. The extensive irradiation of triazine XXXa slowly afforded carbazole.

Photolysis of the precursor triazine XXXd gave a remarkably stable benzhydrylideneamino-3H-2,1,3-benzoxathiazole (XLIIId) whose structure was established on the basis of spectral data. In this case it appeared that 2-benzhydrylideneamino-2H-benzothiazete-1,1-dioxide (XXXId) also was an intermediate which subsequently rearranged to the benzoxathiazole XLIIId at a low temperature.

2-t-Butyl-2H-benzothiazete-1,1-dioxide (XXXIb) was not formed during the photochemical decomposition of a possible precursor triazine XXXb.

LITERATURE CITED*

1. F. G. Mann and F. H. C. Stewart, J. Chem. Soc., 2826 (1954); M. P. Cava and A. A. Deana, J. Amer. Chem. Soc., 81, 4266 (1959); L. A. Errede, ibid., 83, 949 (1961); W. Baker, J. F. W. McOmie and D. R. Preston, J. Chem. Soc., 2971 (1961); K. Sisido, Y. Udo and H. Nozaki, J. Org. Chem., 26, 584 (1961); F. R. Jensen and W. E. Coleman, J. Amer. Chem. Soc., 80, 6149 (1958); M. P. Cava and R. L. Shirley, ibid., 82, 654 (1960); W. Baker, J. F. W. McOmie, G. A. Pope and D. R. Preston, J. Chem. Soc., 2965 (1961).
2. E. Vogel, W. Grimme and S. Korte, Tetrahedron Letters, 41, 3625 (1965).
3. M. P. Cava, B. Hwang and J. P. Van Meter, J. Amer. Chem. Soc., 86, 525 (1964).
4. S. B. Cavitt, H. Sarrafizadeh and P. D. Gardner, J. Org. Chem., 27, 1211 (1962).
5. A. Merijan, B. A. Shoulders and P. D. Garner, ibid., 28, 2148 (1963).
6. A. B. Turner, Quart. Revs., 18, 347 (1964).
7. E. M. Burgess and L. McCullagh, J. Amer. Chem. Soc., 88, 1580 (1966).
8. M. Fischer and F. Wagner, Chem. Ber., 102, 3486 (1969).
9. M. Fischer, Chem. Ber., 102, 3495 (1969).
10. R. Gomper and H. D. Lehmann, Angew. Chem. Intnat. Ed., 7, 74 (1968).
11. E. M. Burgess and G. Milne, Tetrahedron Letters, 93 (1966).
12. G. Ege and E. Beisiegel, Angew. Chem. Intnat. Ed., 7, 303 (1968).
13. L. A. Paquette and T. R. Phillips, J. Org. Chem., 30, 3883 (1965).
14. D. C. Dittmer and N. Takashina, Tetrahedron Letters, 50, 3809 (1964).
15. D. C. Dittmer, R. S. Henion and N. Takashina, J. Org. Chem., 34, 1311 (1969).

*

For the complete titles of all journals referred to, see Chemical Abstracts, 55, IJ (1961).

16. J. F. King, K. Piers, D. J. H. Smith, C. L. McIntosh and P. deMayo, Chem. Comm., 31 (1969).
17. J. F. King, A. Hawson, D. M. Deaken and J. Komery, ibid., 33 (1969).
18. R. W. Hoffmann and W. Sieber, Angew. Chem. Internat. Ed., 4, 786 (1965).
19. R. W. Hoffmann and W. Sieber, Annalen, 703, 96 (1967).
20. R. Willstatter and F. Muller, Chem. Ber., 41, 2580 (1908).
21. N. E. Heimer and L. Field, J. Org. Chem., 35, 1668 (1970).
22. Values taken from T. L. Cottrell, "The Strength of Chemical Bonds," Cornell University Press, Ithaca, N. Y., 3rd ed., 1960, or estimated from Pauling's formula.
23. The author is grateful to Professor B. M. Gimarc for his computing the delocalization energy in this table.
24. Parameters used for:

Couloumb Integrals: $\alpha_x = \alpha_c + h_x \beta_{cc}$
 Resonance Integrals: $\beta_{xx} = k_{xx} \beta_{cc}$

For IIa

$h(N) = 1.5$
 $h(O) = 2.0$
 $h(S) = 1.0$

$k(C-N) = 0.8$
 $k(C-O) = 0.8$
 $k(C-S) = 0.6$
 $k(O-O) = 0.8$
 $k(N-N) = 1.0$
 $k(S-S) = 0.5$

For IIb

$h(N) = 0.5$
 $h(O) = 1.0$
 $h(S) = 0.5$

$k(C=N) = 1.0$
 $k(C=O) = 1.0$
 $k(C=S) = 0.9$
25. F. Ullmann and C. Gross, Chem. Ber., 43, 2694 (1910).
26. N. L. Smith, J. Org. Chem., 16, 415 (1951).
27. F. Kehmann and J. H. Dardel, Chem. Ber., 55, 2349 (1922).
28. R. J. W. Gremly, J. Chem. Soc., (C), 1229 (1966).
29. L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons Inc., New York, 1967, p. 20.
30. E. M. Burgess, R. Carithers and L. McCullagh, J. Amer. Chem. Soc., 90, 1923 (1968).

31. R. L. Hale and L. H. Zalkow, Tetrahedron, 25, 1393 (1969).

VITA

Meng-sheng Ao was born June 24, 1936 in Pescadores, Formosa. He received the Bachelor of Science degree in Biology in 1960 from Taiwan Normal University, Taipei, Taiwan. Following graduation he was employed as teaching and research assistant for his alma mater and the Zoological Institute of Academia Sinica of China. He entered the University of Iowa at Iowa City, Iowa for further study in biochemistry and chemistry in 1964. He began graduate study in organic chemistry at the Georgia Institute of Technology in September , 1966.

He is married to the former Ming-ju Tsaur.